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(54) Title: POLYMERIC COMPOSITIONS RAPIDLY HEATABLE UNDER ELECTROMAGNETIC IRRADIATION, THEIR USES AND PROCESSING METHODS

(57) Abstract: Thermoplastic polyolefin compositions capable of undergoing particularly rapid and uniform heating under microwave irradiation, or under simultaneous microwave and infrared irradiation. Processes for conversion of such thermoplastic compositions into semifinished articles, and subsequent and fast hot conversion thereof into finished articles of various type under microwave irradiation, or under simultaneous microwave and infrared irradiation.



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POLYMERIC COMPOSITIONS RAPIDLY HEATABLE UNDER
ELECTROMAGNETIC IRRADIATION, THEIR USES AND PROCESSING
METHODS

5 The present invention relates to polymeric compositions endowed with strong electromagnetic absorption capabilities over the frequency intervals of microwave and infrared radiations.

More particularly, the present invention relates to thermoplastic polyolefin compositions, optionally post-crosslinkable, comprising additive systems capable of
10 making the polyolefin materials of conventional industrial use heatable with notable rapidity and uniformity under either microwave irradiation or simultaneous microwave and infrared irradiation.

Such polymeric compositions are devoted to the manufacture of a variety of finished or semifinished articles with a polyolefin material, whose controlled and
15 particularly fast heating, or a controlled and particularly fast heating of portions of which ones, is necessary or advantageous during the relevant manufacturing or post-manufacturing processes. In this context, the present invention describes also the preparation processes of said compositions, and the conversion processes of semifinished articles prepared from said compositions into finished articles by fast
20 heating by microwave irradiation, or simultaneous microwave and infrared irradiation, and simultaneous or immediately subsequent hot deformation or hot forming by application of mechanical stresses as well known in the field of plastic materials processing.

The very broad range of industrial uses of polyolefin-type plastic materials for the
25 manufacture of a multitude of finished articles and components, for both conventional and many and different technical, civil and industrial, applications have been well known since decades ago, and are still growing. The large volumes being produced and used, and the large diversification of practical uses, of this kind of thermoplastic polymeric materials, as well as the variety of processing technologies applicable to them,
30 are justified by the advantageous combination of features being proper to said materials: lightness and, above all, favorable ratios between the values of their mechanical properties (stiffness and yield strength) and density, complete insensitivity to water, excellent chemical resistance (except to a relatively few and particularly aggressive

chemical agents) and to most organic solvents except hydrocarbons, excellent dielectric properties, and low cost.

The class of polyolefin materials embraces a remarkable variety of products, the most important of them being homo-, co-, and ter-polymers of ethylene, propylene, 1-butene, 4-methyl-1-pentene and other α -olefins. The relevant intrinsic and applicative features are extensively reviewed in several publications, such as, for example, in the series of monographs of different authors published in the "Encyclopedia of Polymer Science and Engineering", 2nd edn., J. Wiley & Sons, New York, 1986, volume 6, from page 383 to page 564, the contents of which should be considered herein incorporated as references.

In the manufacture of the widest variety of finished articles, semifinished articles and components with polyolefin materials, it is possible to use the broadest range of processing technologies applicable to thermoplastic polymeric materials in general, among which the following ones are worth mentioning by virtue of their importance: injection molding, extrusion and drawing of continuous bodies having a different cross section geometry, such as pipes, tubes, thin tubes, bars, rods and slabs, extrusion and calendering of slabs and sheets, extrusion and blowing of tubular films, blow-molding of hollow bodies in the molten state in a mold, fiber spinning and stretching, melt forming of hollow bodies of considerable size in molds describing multiaxial rotations (technique being known in the Anglo-Saxon terminology as "roto-molding"), and so on. In the industrial practice, many of such semifinished articles, attainable in this way with the different polyolefin materials, are furthermore and frequently submitted to various continuous or discontinuous, cold or hot post-processing treatments.

As known to those skilled in the art, many important hot post-processing treatments on these materials are feasible with suitable efficiency, rapidity and consistency only after, or in conjunction with, a preheating of the semifinished article or component up to a temperature close or equal to the softening temperature, or even the melting temperature, of the particular polymeric material being involved. Particularly, although not exclusively, said post-processing treatments are concerned with semifinished articles, particular volumetric portions of them, components or relevant portions thereof, having a significant thickness, whose order of magnitude is of from one to several millimeters, and, sometimes, even from one to several centimeters.

Hot post-processing operations of this kind are shape and/or size modifications, or

even modifications of the sole aspect ratios of semifinished articles, portions or components thereof. The onset of softening, or the true softening, of the polymeric material enables it to undergo easily and rapidly, as well as to maintain after the material cooling and solidification, the shape or aspect ratio modification being imparted to the object through the different kinds of post-processing treatments by a particular mechanical stress or combination of different, simultaneous or subsequent, mechanical stresses. The examples of such discontinuous, hot post-processing operations are numerous, and the following ones can be mentioned among them: pipe and tube bending; necking or flaring of short end-portions of pipe segments for fabrication of bell and spigot joints; thermoforming of sheets or slabs (having a uniform thickness, or yet having a thickness locally differentiated zone by zone) in shaping molds, for the manufacture of open containers, shaped panels, and so on, of various shapes and uses, as shown, for instance, in US patents 4,141,771 and 4,220,683.

The examples of similar continuous hot post-processing operations are numerous and important as well, including the following ones being of particular industrial interest: thermoforming of continuous straps and strips into profiles having a different open cross section (with L, U, V, Z-shaped section, and so on); conversion of sheets or slabs of uniform thickness into sheets and slabs having a thickness locally differentiated zone by zone; uni - or bi-axial stretching of sheets; axial stretching of extruded, small-diameter rods or tubes, and yarns or filaments, as shown in US patent 3,173,977, and still others. Further and particularly important, continuous hot post-processing operations of said kind include the following ones: a) formation of nets, grids, geo-nets and geo-grids by uni- or bi-axial stretching of extruded (or extruded and then calendered) sheets or slabs endowed with predetermined and ordered spatial patterns of die-cut and variously shaped holes, or appropriate localized punched depressions, as disclosed, e.g., in US patents 4,303,714, 4,374,798, 4,574,100, 4,590,029, 4,618,385, 4,652,409, 4,743,486, 5,419,659 and 6,423,394; b) semi-discontinuous molding of open containers of various shape having grid walls by die-drawing of slabs or sheets endowed with holes or localized depressions like those mentioned above, as shown in US patent 4,394,342; c) manufacture of various network structures having a sheet-like structure such as the aforementioned nets, grids, geo-nets and geo-grids, or like them though bearing protrusions orthogonal to the plane, or also being properly tridimensional, by uni- or bi-axial stretching of "preforms" having a bi- or tri-dimensional network

structure and various and even involved geometry, "preforms" being directly obtained by continuous, dynamic extrusion or co-extrusion processes, or also by multiple extrusion combined in a plurality of directions, as better shown in the following and described for example in UK patent 880,236, as well as in US patents 4,711,751, 5,667,869, 5,851,089
5 and 5,891,549.

In all the discontinuous or continuous processes mentioned above, both the heating rapidity and the volumetric heating uniformity of the material, or of part of the same, being subjected to the simultaneous or immediately subsequent hot post-processing operation, are of great and critical technological importance. As known to those skilled
10 in the art and shown in the aforementioned patents, the actual industrial application of such hot working operations to process thermoplastic polyolefin materials is feasible in practice with times being required to heat the polymeric material from room temperature, or from a temperature slightly higher, up to temperatures of 60-130°C typically of the order of one minute, and up to 2-3 minutes at most, and preferentially
15 within one minute. Said industrial application is the more convenient, from the standpoint of the output of finished articles in discontinuous processes and the delivery speed of semifinished articles in the continuous ones, the more said heating time is short.

As well known, it is a general feature of all polymeric materials a low thermal conductivity, much lower than that of the majority of the other materials of conventional
20 use (on average, 50% lower than the conductivity of glasses and ceramics, and several orders of magnitude lower with respect to metals, metal alloys, graphite, and so on). This feature opposes the quick and uniform heating of polymeric materials, especially if formed into objects of considerable thickness, by all conventional heating means used in all the aforementioned post-processing operations, i.e. implying heat transmission from
25 the outer surfaces to the core of the same objects: hot air, steam, hot gases, or mixtures of hot gases and steam such as combustion smokes of gaseous hydrocarbons; hot liquids (such as hot water, by which temperatures of about 95-98°C of the articles to be processed cannot obviously be exceeded); contact with metal, glass or ceramic surfaces, heated by any means. A further and potentially highly efficient heating means, though
30 still conventional according to what said above, is heating by electromagnetic radiation in the range of infrared frequencies. Dealing with such a heating method, however, the following conflict does exist: those materials intrinsically not absorbing such radiation can be penetrated deeply, but they are not heatable; those materials strongly absorbing

the same radiation heat up very much, but only on their surface and for a very limited depth. In this sense, infrared irradiation does not offer significant advantages over the other aforementioned heating methods.

At least in principle, all the conventional heating techniques cited so far can lead to the short heating times of the core of the materials, having a low thermal conductivity, being required or desired according to what said above, but only after having submitted the surfaces of the semifinished articles, or portions thereof, to temperatures much higher than those actually reached, instant by instant, in the material core, with overheating risks which almost all polymeric materials (and particularly the polyolefin ones) cannot sustain, from both a physical standpoint (early melting of the surface layers) and a chemical one (degradations, up to materials pyrolysis). This limits, by necessity and remarkably, the velocity of hot working operations in this kind of processes.

As known to those skilled in the art, very efficient heating means for dielectric materials such as the polymeric ones, potentially very fast and acting deeply into the materials themselves, is electromagnetic irradiation by microwaves or radio frequencies, and preferentially microwave irradiation, which is more powerful and versatile. The principles and industrial devices pertaining to these heating techniques are extensively described, for instance, in the book "Industrial Microwave Heating", by A.C. Metaxas and R.J. Meredith, published by Peter Peregrinus Ltd, London, 1983 (and relevant 1993 reprint), and in the volume "Dielectric Heating for Industrial Processes", published by UIE – Union Internationale pour les Applications de l'Electricité, Paris, 1992, the contents of which are entirely incorporated herein as references. The theoretical and practical aspects of the same technologies applied or applicable to polymeric products are specifically reported in the monograph "Physics and Chemistry of Microwave Processing", by F. Parodi, in the treatise "Comprehensive Polymer Science", 2nd supplement, pages 669-728, published by Pergamon-Elsevier Science Publishers, Oxford, 1996, publication the contents of which are also herein incorporated as references. According to what disclosed in the above-mentioned publications and in the text "Classification of electromagnetic radiation" in the volume "Handbook of Chemistry and Physics", 76th edn., CRC Press, Boca Raton, Florida (USA), 1995-96, pages 10-291—10-292, the frequency ranges of electromagnetic radiation defined as radio waves or microwaves are specified according to international agreements as

hereinafter indicated. Radio waves: frequencies from 3 kHz to 300 MHz. Microwaves: UHF frequencies (300 MHz – 3 GHz) and SHF frequencies (3-300 GHz); EHF frequencies (30-300 GHz), better known as “millimetric waves”.

Similarly to radio frequency processes, the direct applicability of microwave heating to polymeric materials processing is exclusively limited to those polar polymers possessing sufficient intrinsic absorption capabilities of said radiation. Useful applications of this technique for hot post-processing of polar polymers, as those mentioned above, are shown, e.g., in US patents 3,364,294 and 4,497,759.

Unfortunately, as known, polyolefin polymers are generally characterized by both an almost complete transparency to microwaves and radio frequencies, and modest infrared absorption capabilities, thus resulting substantially non-heatable by microwave or radio frequency irradiation, and very slightly heatable by infrared irradiation. In order to make heatable and thus processible by microwave or radio frequency irradiation those polymeric material (in particular polyolefins) being insensitive to these radiation, it is already known to the experts the possibility of incorporating additives having inherent and strong microwave and/or radio frequency absorption capabilities or, alternatively, being capable of endowing the polymeric host-material with said features by converting it into a semiconductor or weak electric conductor capable of dissipating energy through internal circulation of electric currents induced by said radiation. Each one of such additives (commonly defined as microwave or radio frequency absorption “susceptors”) shows, however, significant drawbacks and limitations, particularly in fields and processing technologies being even slightly different from those strictly claimed and disclosed case by case. Said additives include, for example, the hereinafter listed products:

- a. Carbon powders of different kind, and above all carbon blacks of the various kinds, graphite and coke carbon powders, and so on. Among such weakly electroconductive powders, carbon black is being used since decades ago in rubber compounds. As an example of carbon black use as a susceptor additive for microwave heating of plastic materials being feebly sensitive, or insensitive at all, to said irradiation is that reported in US patent 5,338,611. High amounts of these additives are required in order to get sufficient heating capabilities as under microwave as under radio frequency irradiation: in practice, never less than 10% by weight, and often more than 20%. These weight percentages are equivalent to

very high volume percentages of these powders, causing strong melt-viscosity increases of polymers, and therefore significantly worsening the processability of the so-filled materials, often associated with worsening of their mechanical properties.

- 5 b. Polar, polymeric and non-polymeric, organic components. Examples of uses of additives of this kind in polyolefins and other nonpolar polymers are those disclosed in US patents 4,288,399, 4,360,607 and 4,840,758. These additives are intrinsically incompatible, or are scarcely miscible, with the nonpolar polymers which they are added to (thus causing internal inhomogeneities, and worsening
10 their mechanical properties), and many of them (e.g. alkanolamines, glycols and polyglycols) are hygroscopic, water-soluble products, and can be extracted by water from filled materials.
- c. Mineral powders. Some of these additives have been described as effective, although only limitedly to the radio frequency heating technique: particular grades
15 of zinc oxide, bentonites and zeolites, as in US patent 4,661,299; titanium or zirconium hydroxyethylphosphonates and acid phosphates, as in US patent 4,721,738.
- d. Metal powders and metal-coated mineral powders. By virtue of their high electric conductivity, they are the only truly effective additives whenever intense and fast
20 heating effects are required. Examples of applications of this kind have been reported in US patents 4,972,058, 4,959,516, 5,021,293 and 5,254,824. These applications disclose polymeric compositions which can be strongly heated by microwave irradiation in a few tens of seconds, though only with amounts of metal or metal-coated powders (in particular, aluminum powders) ranging in practice
25 from 20 to 50% by weight and over. As already said, these so high amounts of dispersed metal powders can guarantee the high heating rates being desired, but create other undesirable effects such as, in particular: 1) drastic reductions of mechanical properties of materials (in particular, remarkable toughness reductions), which are primarily linked to poor metal-to-polymer adhesion; 2) a big tendency to
30 generate harmful, and even dangerous, electric surface discharges under microwave irradiation, this tendency being potentially governed by diminishing the metal powder amount and/or the irradiation intensity, though depressing precisely in this way the materials heating rates.

In front of the potential of microwave or radio frequency irradiation for heating rapidly and deeply those materials intrinsically being, or being made, sufficiently capable of absorbing such radiation, these heating techniques are nevertheless affected by the two specific and well-known applicative limitations outlined in the following:

- 5 1) In conjunction with the quick heating of their inner portions, the surface of objects irradiated in air at room temperature inevitably tends to remain, exactly contrary to what happens with all the other heat transfer techniques, at temperatures notably lower than those reached instant by instant in the material core during the heating process (some and often several tens of degrees centigrade lower). As well known,
10 this is due to fast heat losses the surfaces and surface layers of the material undergo by irradiation and convection towards the atmosphere external to the objects irradiated. In practice, this tends to greatly limit the possibility of a fast and intense heating of thin objects, such as sheets of thickness below 1-2 mm, being characterized by high surface-to-volume ratios. This technological limitation is
15 well known and recognized from decades in the field of microwave vulcanization of extruded rubber profiles (application for which the use of heating tunnels combining microwave heating and forced circulation of high-temperature air is well established since the seventies of the past century) and well expressed, for instance, in the publications mentioned above and incorporated as references, as well as in
20 the already cited US patent 4,497,759. The only solution universally adopted to alleviate this drawback is the use of hot air or other hot gases as a supplementary source of conventional heating, capable of compensating for, or at least attenuating, such heat losses from surfaces.
- 25 2) In spite of the remarkable and general efficiency of microwave heating (as well as the radiofrequency one), the temperature distribution within irradiated objects, and particularly within those of significant or remarkable thickness of several millimeters or even centimeters, tends to be notoriously very inhomogeneous layer by layer of the material, because of a superposition of simultaneous effects. Even in irradiated objects of simple shape, the true distribution profiles of internal and
30 surface temperature values are different case by case, and variable in time during the same irradiation process, depending on the following main parameters: device features and irradiation conditions; intrinsic radiation absorption capabilities of the material, and their temperature dependence; material thickness; object shape. This

situation is even more complex in the case of objects having asymmetric shapes, different thickness in different areas, and so on. This behavior, easily verifiable by experimental methods, is described and analyzed in several publications, among which the following ones can be cited as examples: “Analysis of microwave heating of materials with temperature-dependent properties”, by K.C. Ayappa et al., AICHE Journal, 1991, vol. 37, N° 3, pages 313-322; “Heat transfer modeling in a polymer sample located in a microwave field”, by A. Joly et al., Journal of Thermal Analysis, 1993, vol. 39, pages 1285-1296. Also this technological inconvenience can be limited, at least partially, according to the known industrial practice, by balancing the internal temperature inhomogeneities by hot air or other hot gases forced to flow around the semifinished articles or components being submitted to microwave irradiation.

The industrial necessities of compensating for the heat losses from surfaces and the internal temperature inhomogeneities of the objects irradiated by large volumes or strong streams of hot air or hot gases in microwave irradiation ovens, attenuates or cancels the energy savings attainable through the microwave heating technology, besides making more complex and expensive the devices needed.

In US patent 6,231,803 a method is disclosed for the hot stretching, under pure microwave or radio frequency irradiation, of nets or grids made of polyolefin materials filled with any known additive capable of making polyolefin polymers able to absorb such radiation, without the necessity of using any conventional supplementary heating means whose simultaneous use in combination with microwave or radio frequency irradiation is being recognized as necessary, and adopted in the industrial practice according to the previous state of the art, to balance the surface heat losses and the spatial inhomogeneities of internal temperature of the so-irradiated objects, as said above. This patent affirms an unexpected and surprising temperature homogeneity of the articles produced with the filled polyolefin materials heated in ovens solely acting by microwave irradiation, irrespective of their geometry and thicknesses, and without the necessity of any novel precaution regarding either the material composition or the microwave irradiation device. Unfortunately, such patent does not provide potential technical solutions of broader interest for the aforementioned problems of temperature inhomogeneity, i.e. solutions potentially applicable to the generality of practical situations wherein such problems are well evident, proven and experimentally verifiable.

A potentially very efficient industrial solution, commonly adopted in domestic microwave ovens, optionally in combination with hot air circulation, is the already mentioned irradiation by infrared rays combined with microwave irradiation. For the processing of polyolefins, as already said being scarcely absorptive of infrared radiation, this solution is per se of little efficacy. Carbon black, as an additive able to induce medium microwave heating capabilities, is characterized at the same time by strong infrared absorption capabilities and by the capability to transmit by conduction the heat it has absorbed by infrared irradiation to the polyolefin, which is per se nearly transparent to such radiation. However, such overall infrared absorption capabilities are in practice cancelled by the strong infrared surface emissivity typical of carbon black, graphitic carbon and black bodies in general (quantified by very high values, not lower than 0.95, of their "total emissivity coefficient"), high emissivity which is the main reason of the known and strong surface heat losses by rubber and plastic materials filled with carbon black and heated by microwave (or by radio frequency) irradiation.

Metal powders are additives which, at the same time, can impart to polyolefins a powerful microwave heatability and, thanks to their nice thermal conductivity, can accelerate the internal thermal exchanges by reducing the conventional temperature inhomogeneities within microwave-irradiated materials. Contrary to carbon black and other carbon powders, metals (such as aluminum, copper, silver, bronze, brass, steel, and so on) and metallic paints containing their powders, possess a low infrared emissivity (quantified by values of the "total emissivity coefficient" typically lower than 0.3, and not higher than 0.7 even in the worst cases). This low infrared emissivity tends to minimize (in the desired way in the present ambit) the surface heat dissipations by plastic materials filled with metal powders and heated by microwaves. Representative values to support what said above are reported, for instance, in the compilation "Normal total emissivity of various surfaces" (Table 10-17) published in the volume "Perry's Chemical Engineers' Handbook", 6th edn., McGraw-Hill, New York, 1984.

Unfortunately, metals possess known and strong reflection capabilities of infrared radiation. Thus, their powders dispersed in a polymer in no way can contribute, contrary to carbon black and graphite powders, to the surface heating of the same polymer being irradiated by infrared radiation if it has, as polyolefins, per se very poor absorption capabilities of such radiation. This tends to cancel, in metal powder-filled polyolefins, the possibility of combining useful surface heating effects by infrared irradiation with

the advantageously low heat dissipation features proper to metal surfaces.

The Applicant has now found the possibility of overcoming the aforesaid limitations to the physico-mechanical properties and the hot processability under microwave irradiation of polyolefin materials filled with known microwave-absorbing "susceptors", and this through the use of well-defined additive systems. Such additive systems impart particularly enhanced heating capabilities under microwave irradiation to polyolefin polymers whereinto they are dispersed, allowing, even with a low dosage thereof and under low volumetric densities of irradiation energy as better explained in the following, the fast and optimal post-processing of these materials by means of this heating technique. Moreover, said additive systems increase the absorption capabilities of infrared radiation by polyolefin polymers whereinto they are dispersed, allowing the advantageous combination of heating treatments of their surface layers by infrared irradiation with the heating the their entire mass by microwave irradiation.

It is therefore an object of the present invention to provide thermoplastic polyolefin compositions, containing metal powders, capable of undergoing a very rapid heating when subjected to microwave irradiation, but exempt, by virtue of the modest amounts of the same metal powders they contain, from the known risks of generating electric surface discharges under the influence of such electromagnetic irradiation, endowed with good mechanical features in the solid state, and a nice processability in the molten state as well.

A further object of the present invention is the provision of thermoplastic polyolefin compositions, having the aforementioned features, which can heat up very rapidly as much within their mass as on their surface when simultaneously subjected to electromagnetic irradiation by microwave and infrared radiation.

It is another object of the present invention to provide thermoplastic polyolefin compositions having the aforementioned features, useable for the manufacture of articles, parts or components being rapidly hot post-processable under microwave irradiation or, advantageously, under simultaneous microwave and infrared irradiation, or yet by using a combination of such electromagnetic irradiation treatments with other conventional heating or thermostating treatments.

A further and more particular object of the present invention is the provision of thermoplastic polyolefin compositions suitable for the manufacture of various semifinished articles, and the relevant processing methods for their conversion into

finished articles, parts or components, by discontinuous or continuous hot post-processing operations under the accelerated electromagnetic heating treatments mentioned above, such as: bent pipes and tubes, tubes endowed with end-portions for bell and spigot joints; open containers and shaped panels; profiles having a various
5 open cross section obtained by forming of planar extruded bars; mono- or bi-axially-stretched sheets; stretched rods and thin tubes; nets, grids, geo-nets and geo-grids by mono-or bi-axial stretching of perforated, extruded sheets or plates, and others.

These and other objects can conveniently be obtained by using the thermoplastic polyolefin compositions, disclosed hereinafter and in the 1-41 claims enclosed, by hot
10 forming them into semifinished articles and then subjecting said semifinished articles to fast mechanical deformations in combination with fast microwave heating treatments, with simultaneous microwave and infrared irradiation, or also with microwave irradiation, or with joint microwave and infrared irradiation, combined with different, conventional heating or thermostating treatments, as disclosed hereinafter and in the 42-
15 55 claims enclosed.

It is therefore an object of the present invention the thermoplastic polymeric compositions comprising the following components:

- A. a thermoplastic polyolefin material, consisting of a thermoplastic polymer of polyolefin type, or a physical mixture of two or more thermoplastic polymers of
20 polyolefin type different from each other, optionally in admixture with chemical agents selected from the group consisting of free-radical initiators, catalysts, chemical co-reactants, and/or combinations thereof, suited to promote or initiate the total or partial crosslinking of the polyolefin material, as well as other optional additives and/or auxiliaries of known use, as hereinafter explained;
- 25 B. a metal powder, or a mixture of different metal powders;
- C. a tertiary phosphine or amine, or a mixture of different two or more tertiary phosphines and/or amines, having general formula $ZY_1Y_2Y_3$, wherein Z is a phosphorus or nitrogen atom and Y_1 , Y_2 and Y_3 , equal to or different from each other, are C_6 - C_{18} aryl, C_7 - C_{36} alkylaryl, C_7 - C_{36} alkoxyaryl radicals, mixed C_8 - C_{36}
30 alkyl-alkoxy-aryl radicals, C_9 - C_{24} cycloalkylaryl radicals, mono-, bi- or triaryl-methyl radicals, wherein the aryl radical contains from 6 to 14 carbon atoms, mono-, bi- or trialkylaryl-methyl radicals, wherein the alkylaryl group contains from 7 to 36 carbon atoms, or also mono-, bi- or tri-cycloalkylaryl-methyl radicals, wherein

the cycloalkylaryl group contains from 9 to 24 carbon atoms;

D. an organic or inorganic mono-, di- or polybasic protic acid, or a mixture of two or more different organic and/or inorganic mono-, di- or polybasic protic acids; optionally, said component of the compositions can be not present.

5 Thermoplastic polymers of polyolefin type which can be used as constituents of the component "A" of the compositions of the present invention are the homopolymers of the α -olefins containing from 2 to 18 carbon atoms, copolymers and terpolymers of two or three, respectively, of said α -olefins, different one from the other, copolymers of an α -olefin, as above described, with an unsaturated comonomer of different nature or, yet,
10 the terpolymers of one or two of said different α -olefins with two or one unsaturated comonomers of different nature, respectively.

Therefore, the scope of the present invention comprises, as constituents of the component "A", the various homopolymers of ethylene, commonly known as "low density polyethylene" (LDPE), "medium density polyethylene" (MDPE), "high density
15 polyethylene" (HDPE), "ultra-high density polyethylene" (UHMWPE), as well as the amorphous or semicrystalline copolymers and terpolymers of ethylene containing minor weight portions of α -olefins having a number of carbon atoms typically comprised in the range of from 3 to 18, and conventionally known and sold as "linear low density polyethylene" (LLDPE), "very-low density polyethylene" (VLDPE) and "ultra-low
20 density polyethylene" (ULDPE). The known semicrystalline homopolymers of different α -olefins having a number of carbon atoms higher than two, as well as the various homopolymers of propylene, represented by isotactic polypropylene, syndiotactic and partially iso- or syndio-tactic polypropylene, and isotactic or partially isotactic polybutene-1 and poly-4-methylpentene-1, are being comprised within the scope of the
25 present invention as well.

Other polyolefin-type polymers comprised within the scope of the present invention are: atactic polypropylene, the propylene polymers known as "polypropylene with a high degree of molecular branching", random copolymers of propylene and α -olefins having a number of carbon atoms > 4 , e.g. of from 4 to 12 (as those with butene-1),
30 amorphous or semicrystalline copolymers of ethylene and propylene with a different ethylene-to-propylene ratio and a random or block distribution of both these comonomers, blends of ethylene polymers of the aforementioned different types, polymeric blends among polyethylene and/or polypropylene of the aforesaid different

types and/or the aforementioned ethylene-propylene copolymers, and/or yet the ethylene-propylene-diene terpolymers such as those commonly known as "EPDM rubbers". Constituents of the component "A" according to the present invention are also the linear homo-, co- and ter-polyolefins having a controlled molecular weight
5 distribution, attainable by using the catalysts known to those skilled in the art as "metallocene catalysts", among which, for instance, several copolymers and terpolymers of ethylene with one, or respectively two, linear α -olefins having a number of carbon atoms in the range of from 4 to 18, such as ethylene-butene-1 copolymers and ethylene-butene-1-hexene-1 terpolymers.

10 Copolymers and terpolymers of α -olefins with unsaturated comonomers containing more than one olefinic unsaturation, or one olefinic unsaturation and one or more functional groups, as well as the polymeric products deriving from homo-, co- and ter-polymers of α -olefins through their grafting by comonomers containing both one olefinic unsaturation and one or more functional groups, are further comprised within
15 the scope of the present invention. Said unsaturated comonomers provide said polyolefin materials with free chemical functionalities which can be used to obtain, in combination with their melt-processing or in a subsequent processing step and with the help of free-radical initiators, catalysts and/or chemical co-reactants, a partial or total crosslinking of the polyolefin materials. For example, the following products belong to
20 this list of polyolefin materials:

- a) ethylene polymers (particularly LDPE and HDPE) and ethylene-propylene copolymers grafted with small quantities of vinyltrialkoxysilanes (e.g. vinyltrimethoxysilane), as well as the copolymers deriving from the direct copolymerization of ethylene with a vinyltrialkoxysilane such as
25 vinyltrimethoxysilane; such products are post-curable in the solid state by hot water or steam treatments with the aid of several known catalysts (usually tin derivatives such as dibutyltin dilaurate, dibutyltin diacetate, tin(II) octoate, sulfonic acids and related thermally or hydrolytically-weak salts with amine compounds, various carboxylic acids, and so on) pre-admixed with the molten material;
- 30 b) products attainable by grafting modest weight fractions of vinyl compounds containing epoxy groups (such as glycidylacrylate and glycidylmethacrylate) onto homo-, co- and ter-polymers of α -olefins, such as ethylene and propylene, curable by catalysts and/or curing agents known in epoxy resins chemistry;

- c) copolymers of ethylene with non-conjugated linear dienes such as 1,7-octadiene, 1,9-decadiene and 1,13-tetradecadiene, or copolymers of propylene with branched linear non-conjugated dienes, such as 6-methyl-1,6-octadiene or 7-methyl-1,6-octadiene, copolymers containing free olefinic unsaturations and post-curable
5 through the introduction of free-radical initiators (such as peroxides, peresters, percarbonates and organic azo-compounds) and with the potential aid of modest quantities of several known bi- or tri-functional monomers, such as 1,4-butanediol or 1,6-hexanediol diacrylates or dimethacrylates, neopentylglycol diacrylate or dimethacrylate, trimethylolpropane triacrylate or trimethacrylate, triallyl-cyanurate
10 or -isocyanurate, triallyl-1,3,5-benzenecarboxylate.

Finally, within the scope and the objects of the present invention, the copolymers and terpolymers among one or two α -olefins, respectively, and carboxylic acids containing one olefinic unsaturation, such as, in particular, ethylene-acrylic acid and ethylene-methacrylic acid copolymers, having a total content of said acid comonomers
15 variable, although not higher than 2.5% by weight, can also be used as polyolefin materials for the component "A". Similarly, the polymeric products attainable from homo-, co- and ter-polymers of α -olefins by grafting onto them several monocarboxylic acids containing one olefinic unsaturation, such as acrylic acid, methacrylic acid, monoalkylmaleates or monoalkylitaconates, or anhydrides of unsaturated bicarboxylic
20 acids such as maleic anhydride or itaconic anhydride, and containing an overall portion of such grafting acid agents variable though not higher than 1.5% by weight, are further useable.

The component "B" of the thermoplastic polymeric compositions of the present invention is represented by a metal powder, or a mixture of different metal powders,
25 consisting of small metal particles having a lamellar, acicular, fibrillar, dendritic, spherical, spheroidal, clavicular shape, or having an irregular shape with smooth or crater-rich surfaces, irregular and complex shape such as small cavernous bodies or containing a plurality of microcavities, hollow spherical or spheroidal particles, or a mixture thereof. Metal powders whose particles have a lamellar, acicular, fibrillar,
30 dendritic shape, whose particles are small cavernous bodies or include microcavities, or also and suitably, mixtures thereof or between the latter and powders having particles with spheroidal and/or clavicular shape, can preferentially be used for the scopes of the present invention. Said metal powders can consist of a single metal or an alloy of

different metals, a metal or a metal alloy, whose particles are surface-coated with a thin layer of a second different metal or metal alloy, or yet a non-metallic mineral powder whose particles are surface-coated with a thin layer of a metal or metal alloy.

Among the powders of a single metal, preferentially aluminum, copper, iron, nickel
5 or silver powders, and more preferentially aluminum powders, can be used for the purposes of the present invention. Among the powders of metal alloys, brass powders (i.e. powders of alloys containing a plurality of different metals, but prevalently consisting of copper and zinc), bronze powders (i.e. powders of alloys containing a plurality of different metals, but prevalently consisting of copper and tin in variable
10 ratios), aluminum alloys (such as aluminum-magnesium or aluminum-copper alloys, as well as the aluminum-nickel and aluminum-cobalt alloys comprising the so-called Raney-type alloys) can be used preferentially but not limitedly. Among said powders of metal alloys which can preferentially be used, brass and bronze powders can still more preferentially be used alone or in admixture with aluminum powder or different
15 aluminum powders.

Metal and metal powders among those mentioned above and suitable for the purposes of the present invention, having different particle shapes, sizes and size distribution are industrially produced and generally available for a variety of practical uses, e.g. such as pigments for coatings and inks, reactants for chemical syntheses, for
20 the preparation of explosives and pyrotechnic powders, as electro-conductive fillers for plastic materials and thermosetting resins, in the manufacture of metal components through the known techniques of powder metallurgy, and so on.

Alternatively to, or in combination with, the metal powders or powders of metal alloys disclosed above, metal-coated powders of metals or metal alloys, i.e. powders
25 whose particles are coated by a thin layer of a second and different metal or metal alloy, as well as non-metallic mineral powders whose particles are similarly metal-coated, can advantageously be used within the scope of the present invention. Metal-coated metal or mineral powders of said kinds are produced according to various technologies and generally sold, for instance, as super-efficient electroconductive fillers for the
30 manufacture of light-weight parts or components, made of different polymeric materials, with high electric conductivity or tailored to be used for shielding of electromagnetic interferences and disturbances in electronic devices, for radar shielding, and so on. Non-limiting examples of metal-coated metal or mineral powders which can be used in

the present ambit are: silvered aluminum, copper or nickel powders, aluminum-coated milled glass fibers, glass microbeads or glass microspheres, silvered milled glass fibers, glass microbeads, hollow glass microspheres, glass micro-flakes or simply ground glass powders, silvered mica powders, nickel-plated iron micro-grains, and several others.

5 For the purposes of the present invention, the particles forming the metal powder, or the mixture of different metal powders, representing the component "B" of the present thermoplastic polymeric compositions can have sizes or size distributions widely variable and comprised in the range of from 0.1 to 200 μm . The average particle size of said metal powder or mixture of powders, as measurable by the various general
10 characterization and classification methods of powders known to those skilled in the art, are comprised in the range of from 1 to 100 μm , and preferentially of from 5 to 80 μm .

Component "C" of the thermoplastic polyolefin compositions of the present invention is a tertiary phosphine or tertiary amine, or yet a mixture of two or more different tertiary phosphines and/or amines, corresponding to the previously-defined
15 general formula $ZY_1Y_2Y_3$.

Within the scope of the present invention, said tertiary phosphine or amine, or mixture of two or more different tertiary phosphines and/or amines, can either be solid or liquid at room temperature. For the scopes of the present invention, however, it is preferable that said tertiary phosphine or amine, or mixture of two or more different
20 tertiary phosphines and/or amines, be solid at room temperature and have a melting or complete liquefaction point not higher than 250°C, and still more preferentially be solid up to 50°C and have a melting or complete liquefaction point not higher than 180°C.

Non-limiting examples of tertiary phosphines of general formula $PY_1Y_2Y_3$ (wherein Y_1 , Y_2 and Y_3 have the previously defined meanings) which can
25 advantageously be used in the present invention are the following: triphenylphosphine, tri-*ortho*-tolylphosphine, tri-*meta*-tolylphosphine, tri-*para*-tolylphosphine, tri(4-ethylphenyl)phosphine, (*para*-tolyl)-diphenylphosphine, α -naphthyl-diphenylphosphine, β -naphthyl-diphenylphosphine, α -naphthyl-di(*para*-tolyl)phosphine, (*para*-phenoxyphenyl)-diphenylphosphine, tri(4-ethylphenyl)phosphine, 4-ethylphenyl-
30 diphenylphosphine, tri(3-methoxyphenyl)phosphine, 3-methoxyphenyl-diphenylphosphine, di(4-methoxyphenyl)-phenylphosphine, 3-ethoxyphenyl-diphenylphosphine, 4-ethoxyphenyl-diphenylphosphine, benzyldiphenylphosphine, α -naphthylmethyl-diphenylphosphine, β -naphthylmethyl-diphenylphosphine, 4-

methylbenzyl- diphenylphosphine, benzidryl-diphenylphosphine, α -naphthyl-dibenzylphosphine, di(α -naphthylmethyl)-phenylphosphine, di(β -naphthylmethyl)-phenylphosphine, and mixtures thereof.

Non-limiting examples of tertiary amines of general formula $NY_1Y_2Y_3$ (wherein Y_1 , Y_2 and Y_3 have the previously defined meanings) which can advantageously be used in the present invention are the following: tribenzylamine, tri(4-methylbenzyl)amine, tri(3,4-dimethylbenzyl)amine, α -naphthylmethyl-dibenzylamine, β -naphthylmethyl-dibenzylamine, N-phenyl-dibenzylamine, N-(*para*-tolyl)dibenzylamine, N-phenyl-di(4-methylbenzyl)amine, N-(4-ethylphenyl)-dibenzylamine, N-(4-butylphenyl)dibenzylamine, triphenylamine, tri-*para*-tolylamine, tri-*para*-biphenylamine, N,N-dibenzyl-*meta*-anisidine, N,N-dibenzyl-*para*-anisidine, N-(3,5-dimethylphenyl)-dibenzylamine, N-phenyl-N-(α -naphthylmethyl)-benzylamine, and mixtures thereof.

The tertiary phosphines and amines corresponding to the general formulas $PY_1Y_2Y_3$ and $NY_1Y_2Y_3$ respectively, useable for the purposes of the present invention, can be prepared by various and general practical methods and processes known to those skilled in the field of organic chemical syntheses. For example, the aforesaid tertiary phosphines can be prepared by substitution of the halogen atoms of a phosphorus trihalide (in particular, phosphorus trichloride) or a dihaloarylphosphine (e.g. dichlorophenylphosphine), or yet a halodiarylphosphine (e.g. chlorodiphenylphosphine), by three, two or one organic radical respectively, as those previously cited and defined as Y_1 , Y_2 and Y_3 , by reaction with stoichiometric amounts of one or more Grignard reagents of general formulas Y_1MgX , Y_2MgX and/or Y_3MgX , wherein X represents a halogen atom, preferentially chlorine or bromine.

The aforementioned tertiary amines useable in the present invention can be prepared, e.g., by various practical known processes, by N-arylation of diarylamines, such as diphenylamine, by the appropriate aryl, alkylaryl or alkoxyaryl bromide or iodide, with the aid of alkali metals or strong bases. Similar processes can also be used for the preparation of diaryl-arylmethylamines. N,N-di(arylmethyl)-arylamines can be prepared, for example, by N-arylmethylation of the appropriate N-arylmethyl-arylamines, N-arylmethyl-alkylarylamines or N-arylmethyl-alkoxyarylamines, or by double N-arylmethylation of the appropriate primary arylamines, alkylarylamines or alkoxyarylamines with the appropriate arylmethyl halides (preferentially bromides or

chlorides) in the presence, or not, of weak or medium-strength basic reactants.

Component "D" of the thermoplastic polyolefin compositions of the present invention, component which can be optional but is preferentially present, consists of a mono-, di- or polybasic organic or inorganic protic acid having an acid equivalent weight comprised in the range of from 25 to 8000, preferentially in the range of from 25 to 3000, or of a mixture of two or more different mono-, di- or polybasic organic or inorganic protic acids whose average acid equivalent weight is in the range of from 25 to 8000, and preferentially in the range of from 25 to 3000.

Any mono-, di- or polybasic protic acids whose acid equivalent weight is within the aforementioned limits, and is free from oxidizing properties, can be used in the present invention. Orthophosphoric acid, pyrophosphoric acid and polyphosphoric acids having different concentration expressed as orthophosphoric acid, as well as orthophosphorous acid, can be cited as non-limiting examples of the inorganic protic acids which can be used in the present invention.

The organic protic acids which can be used in the present invention include mono-, di- or polycarboxylic acids, alkane-, arene- and alkylarenesulfonic acids, as well as monoarene- and diarenephosphonic acids.

Monocarboxylic acids which can generally be used without limitations for the purposes of the present invention are the fatty acids having a number of carbon atoms higher than or equal to 6, and preferentially in the range of from 12 to 24, such as lauric, myristic, palmitic, stearic, arachidic, behenic, lignoceric acids and mixtures thereof, as well as mono- or polyunsaturated monocarboxylic acids, among which those having a number of carbon atoms higher than or equal to 18, such as oleic, elaidic, erucic, linoleic, linolenic acids, mixtures thereof and mixtures of the latter acids with the aforementioned saturated monocarboxylic acids. Bi- or polycarboxylic acids which can usefully be employed in the present invention include succinic, maleic, fumaric, itaconic, glutaric and adipic acids, orthophthalic and isophthalic acids, trimellitic acid and pyromellitic acid. Bicarboxylic acids which can advantageously be used in the present invention are also the alkenyl-succinic acids, such as octenylsuccinic, decenylsuccinic and dodecenylsuccinic acids, among which, in particular, the isomers and the isomeric mixtures of 2-octen-1-ylsuccinic acid and 2-dodecen-1-ylsuccinic acid. Other suitable acids for the present invention are alkanesulfonic, arenesulfonic and alkylarenesulfonic acids and, among them, those having a number of carbon atoms

higher than or equal to 6 can preferentially and advantageously be used, and even more preferentially those having a number of carbon atoms in the range of from 12 to 34, such as dodecanesulfonic, hexadecanesulfonic, octadecanesulfonic, benzenesulfonic, para-toluenesulfonic acids, as well as the various isomers of dodecylbenzenesulfonic and benzenedisulfonic acids.

Further other acids useable for the purposes of the present invention are the various polycarboxylic acids having a polymeric nature, providing they have an average acid equivalent weight below the aforementioned limit of 8000, and preferentially lower than 3000. Among said polycarboxylic acids of polymeric nature useable with particular advantages, the following ones can be cited as non-limiting examples: copolymers and terpolymers of α -olefins with unsaturated carboxylic acids such as the ethylene-acrylic acid and ethylene-methacrylic acid copolymers having a weight content of acrylic or methacrylic acid higher than or equal to 5%, and preferentially in the range of from 5 to 25%; oxidized polyethylene, preferentially having a low molecular weight and a high acid number, i.e. having an average acid equivalent weight lower than 1800; various terpolymers of ethylene with a polar vinyl comonomer and acrylic or methacrylic acid, such as ethylene-methylacrylate-acrylic acid, ethylene-vinylacetate-methacrylic acid, and others.

As already said, besides the above-described components "A", "B", "C", and "D", the thermoplastic polyolefin compositions being an object of the present invention can optionally contain, as constituents of component "A", various additives and auxiliaries, as well as mixtures thereof, having a nature and use well known to the experts in the field of plastic materials. Said additives and auxiliaries can be added to the composition in order to obtain polymeric materials endowed with particular and specific features for the various applications (e.g. to increase defined mechanical properties such as stiffness, toughness, dimensional stability under prolonged and static mechanical stresses, in order to impart flame retardancy, to improve thermal, oxidative and light stability, and so on), in order to improve their processability, or simply to decrease their cost.

Among those known in the art, the following additives can be used in the present invention, alone or in admixture thereof: powders of mineral fillers; continuous, chopped or milled glass fibers, carbon or polyaramid fibers, fibers spun from natural glasses and other known mineral fibers; lubricating powders; inorganic or organic flame retardants; inorganic pigments; organic pigments; plasto-soluble dyes; thermal

antioxidants; light stabilizers; demolding agents; sliding agents; organic antistatic agents; adhesion promoters, and further other additives and auxiliaries the use of which is known in the art.

As already set forth, the component "A" of the present compositions can also and
5 optionally contain, possibly in combination with the aforementioned additives and auxiliaries, chemical agents selected among free-radical initiators, catalysts, chemical co-reactants and/or mixtures thereof, aimed at promoting or causing the partial or total crosslinking of the polyolefin material itself. Said chemical agents, additives and auxiliaries of known use, optionally added to the polyolefin compositions of the present
10 invention, must be considered as integral constituents of the thermoplastic polyolefin material above identified as the component "A", the overall dosage of which in said compositions should always be considered as comprehensive of said optional chemical agents, additives and auxiliaries.

The thermoplastic polyolefin material, or component "A", of the compositions of
15 the present invention is part of the same compositions for a portion being comprised within the range of from 57 to 99% of their total weight, and preferentially in the range of from 75 to 95% by weight. Within said weight percentage limits, the component "A" of the present compositions may contain, by itself, a variable, overall portion of the additional chemical agents, as well as of the optional additives and auxiliaries been
20 mentioned above, in any case not higher than 50% by weight, and preferentially not higher than 35%, of its own overall weight portion in the same compositions of the invention.

The metal powder, or mixture of metal powders, above identified and described as the component "B", is present in the compositions of the present invention in a
25 percentage ranging from 0.9 to 25% of the total weight of the compositions, and preferentially in the range of from 3 to 10%, while the tertiary phosphine or amine (or the mixture of different tertiary phosphines and/or amines), identified as the component "C", is present in the same compositions of the invention in an amount ranging from 0.1 to 8%, and preferentially from 0.5 to 5%, of the total weight of the same compositions.

30 The protic acid, or mixture of different protic acids, identified as the optional component "D", is present in the compositions in a weight percentage of the entire composition such that its number of acid equivalents be in the range of from 0 to 200%, and preferentially in the range of from 25 to 100%, of the total number of tertiary

phosphine or amine equivalents, or also of the sum of tertiary phosphine and amine equivalents, being contained in the weight portion of the component "C" used in the composition. In all cases, the weight percentage of said acid component "D" cannot exceed, in the present polyolefin compositions, the value of 20%, and preferentially of 10%, referred to the whole compositions.

As reported above, the compositions of the present invention are devoted to be formed and advantageously converted into objects, finished parts or components made of plastic material through a variety of processes which are still an object of the present invention, and comprise the following essential steps:

- i) mixing components "B", "C" and "D" with component "A" in the molten state;
- ii) forming the composition in the molten or plastic state, followed by solidification through natural or artificial cooling, into a semifinished article by a proper forming technology selected among those known for plastic materials processing;
- iii) placing the solid, semifinished article in, or passing it through, a microwave heating device operating with a radiation frequency in the range of from 0.3 to 30 GHz, or a simultaneous microwave and infrared radiation heating device, with simultaneous or immediately subsequent application of mechanical stresses in order to accomplish the hot forming or molding of the object, or a part thereof, in a desired way;
- iv) extracting or driving off the object processed, and yet hot, from the device, followed by natural or artificially accelerated cooling thereof.

In step (i) of said processes, the thermoplastic polyolefin compositions of the present invention can be prepared in accordance with a broad variety of methods. As non-limiting examples, suitable processes are those based on the direct incorporation of the components "B", "C" and "D", as well as of the aforementioned ancillary chemical agents, additives and auxiliaries, in the thermoplastic polyolefin polymer (or mixture of various thermoplastic polyolefin polymers) from which the component "A" is being totally or partially made, in the molten state. Potential, alternative embodiments are different, and the following ones can be cited among them: a) dry-premixing of all the different components followed by melting of the solid pre-mixture, and thorough mixing of all the components in the molten state in a hot mixing device for polymers; b) dispersing components "B", "C" and "D", as well as the aforementioned ancillary chemical agents, additives and auxiliaries, into the polyolefin polymer already heated

and brought to its molten state; c) dispersing the components "B", "C" and "D" in the entire component "A" (already comprising the aforementioned ancillary chemical agents, additives and auxiliaries) being previously molten.

According to a preferred embodiment of the present invention, the components
5 "B", "C" and "D" are incorporated and dispersed, by a hot mixing device, into a fractional portion of component "A" (or yet into a fractional portion of one or a mixture of the thermoplastic polyolefin polymers being part of said component "A") in the molten state, thus obtaining a suitable "concentrate" of the "B + C + D" system of components. Said "concentrate", solidified and granulated or powdered, is used (in
10 place of the separate components "B", "C" and "D") to prepare the complete and final composition desired by one of the above-described methods, by mixing and dispersing it into either the remaining portion of the component "A" or the relevant remaining constituents. The aforementioned fractional portion of component "A" (or of one or a mixture of the thermoplastic polyolefin polymers being its constituents) may be varied
15 at will within broad limits, although it is typically comprised within the range of from 1/20 to 1/2, and preferentially of from 1/10 to 1/5, of the total weight of the whole component "A" in the final composition.

According to a further and convenient embodiment, the components "C" and "D", or yet the component "C" and a portion of the overall amount of component "D" of the
20 selected composition, are separately premixed, and said premixture, preferentially solid at room temperature and converted into granules or powder, is subsequently used for the preparation of the above-described "concentrate" of components "B + C + D", or yet used for the direct preparation of the final composition according to one of the methods described above. The "C + D" or "C + part of D" premixture can be prepared by
25 various methods, i.e., for instance, by direct cold or hot mixing of "C" and "D", optionally aided by a solvent or liquid dispersant which can subsequently be removed, for example by distillation.

A target of maximum importance in the choice and implementation of the processes for the preparation of the compositions of the present invention is the necessity of
30 obtaining and guaranteeing an intimate intermixing of all the components previously described and listed, and, in particular, of obtaining and guaranteeing a fine and homogeneous dispersion of the metal powder, or the various metal powders, being the aforementioned component "B", within the polymeric material being the component

“A” of the same compositions. As well known to those skilled in the field of plastic materials processing, a wide choice is available of mixing devices for molten polymers and molten polymers filled with additives such as mineral and metal powders and fibers, as well as auxiliaries of different nature and purpose such as those previously cited, 5 suitable to prepare the compositions of the present invention, and particularly to guarantee the fine and homogeneous dispersion of their constituents and their fine intermixing being required as said above.

Continuous mixing devices for polymeric materials in the molten state which can advantageously be used for the preparation of the compositions of the present inventions 10 are: twin-screw extruders with co-rotating and intermeshing screws, twin-screw extruders with counter-rotating and intermeshing screws, twin-screw extruders with counter-rotating and non-intermeshing screws. Alternative versions of devices of the latter kind, still suitable to the purposes of the present invention, are the twin-screw extruders with counter-rotating and non-intermeshing screws bearing mixing rotors 15 conventionally known as Banbury-type rotors, devices known as “continuous mixers” for plastics and rubber compounds. Other continuous mixing devices useable in the present invention are single-screw extruders and, among them, particularly those having a screw bearing specific rotary elements with mixing effects, or yet those endowed with downstream static labyrinth-type mixers. Specialty single-screw extruders, the use of 20 which is particularly convenient for the preparation of the compositions of the present invention, are also those endowed with static elements aimed at disrupting the flow of molten material (consisting of pins radially protruding from the wall of the chamber towards the screw axis, and placed in connection with appropriate sector cuts on the coils of the screw itself), as well as those of such a kind operating simultaneously with a 25 reciprocating axial motion of the screw (known as “co-kneading extruders”).

The first surprising advantage of the present polyolefin compositions, with respect to similar traditional compositions consisting of a polyolefin material containing metal powders dispersed therein, is represented by the easiness and rapidity by which the metal powder is being incorporated and homogeneously dispersed into the molten 30 polyolefin material, as well as by the good polyolefin-metal micromechanical cohesion spontaneously occurring in the present compositions solidified upon cooling. This occurs without the necessity of adding any auxiliary dispersants and/or adhesion promoters, which is conversely a common practice known to the experts for this kind of

multiphase materials. This good mechanical cohesion of the present polyolefin-metal powder compositions appears immediately evident through the difficulties of scraping off the metal powder from the surfaces of the pieces fabricated with the same compositions.

5 These advantageous characteristics of the present compositions are probably linked to unexplored dispersing effects and surface adhesion capabilities between the metal (material having a high surface tension) and the polyolefin (nonpolar material with a low surface tension), proper to the "C + D" system of components.

10 For the accomplishment of step (ii), i.e. forming a semifinished article made of the thermoplastic compositions of the present invention, several technologies among those known in the field of processing of thermoplastic polymeric materials can be used. The choice of the technology, relevant devices and working conditions are dictated by the kind of semifinished article. Non-limiting examples of the scopes of the present invention are the variously shaped semifinished articles of finite dimensions which can
15 advantageously be fabricated in a discontinuous way by injection molding, and those attainable by sectioning (for example, by cutting) continuous, semifinished articles such as extruded or co-extruded (as well as extruded or co-extruded and then calendered) semifinished pieces, and optionally cold processed in different ways, better defined in the following. Semifinished articles of these kinds can be for instance: planar pieces or
20 variously shaped portions of flat, embossed or punched slabs or sheets; portions of slabs or sheets having localized and predetermined thickness differences, such as depressions of appropriate shape and depth; pieces of extruded pipe; pieces of solid or hollow extruded profiles having open or closed section of the most different kinds (optionally holed, turned, milled, and so on), and many others.

25 Still to the purpose of providing non-limiting examples, continuous semifinished articles, attainable from the compositions of the present invention and post-processable according to the fast processing methods still being comprised within the scope of the present invention, can be those which can advantageously be fabricated by means of known extrusion technologies, by extruding a single thermoplastic polymeric
30 composition or by co-extruding two or more different thermoplastic polymeric compositions. Said attainable extruded or co-extruded semifinished articles are very diversified, such as, for example, pipes, tubes or thin tubes; solid or hollow extruded profiles, having different open or closed section of a more or less complex shape; films,

5 sheets or slabs; objects having a cylindrical, prismatic or planar geometry, and even a very complex shape (including cavities, depressions or protrusions) attainable by either using extrusion or co-extrusion dies having multiple orifices, or "dynamic" extrusion or co-extrusion dies having a plurality of orifices (rotary dies, describing reciprocating rotary motions, describing reciprocating orthogonal and/or axial motions), such as for instance the "preforms" for nets, grids, geo-nets, geo-grids and other aforementioned bi- or tri-dimensional network structures disclosed, for example, in the already cited US patents 3,654,034, 3,791,784 and 3,874,834. The extrusion or co-extrusion of semifinished articles can optionally be followed by various hot or cold, continuous or
10 semi-discontinuous, processes. Examples of said hot processes are the following ones: calendering, embossing, transit between rolls bearing grooves, being axially toothed, bearing various figures in relief or intaglio figures, punches, dinking dies, and so on. Examples of cold processing operations which can be carried out onto the aforesaid continuous semifinished articles are, for instance, drilling, milling, turning, and others.

15 The microwave irradiation devices (or "applicators") useable for the fast hot post-processing step (iii) on the semifinished articles made from the thermoplastic polymeric compositions of the present invention can be very different from each other from the point of view of technical features, irradiation power, shape and size.

Applicators or microwave irradiation devices (often simply identified as
20 "microwave ovens") of the different kinds useable for the purposes of the present invention are adequately described in the publications mentioned above and herein incorporated as references. In order to exemplify the present invention, without limiting the same, both "resonant cavity applicators" and "waveguide applicators" are included among said microwave devices. In their turn, useable "resonant cavity applicators"
25 include the "multimode resonant cavity" ones, suitable for the widest variety of processes comprised within the present scope, though capable of rather low volumetric densities of irradiation power (Watt/m^3), and the "single-mode resonant cavity" ones (usually cylindrical and small-sized) capable of very high power densities but only usable for post-processing of cylindrical articles, or similar, having a small section.
30 Useable waveguide applicators include the "travelling waveguide" and the "resonant waveguide" ones, as well as all the applicators of such a kind which can give rather high irradiation power densities and which can be implemented according to a variety of schemes known to the experts and thus suitable for a broad variety of kinds and shapes

of semifinished articles, and advantageously useable in the microwave processing of semifinished articles having an elongated shape, or being continuous, and rather small cross section. Further other suitable devices are those implying the direct irradiation of semifinished articles in radiation-confining chambers, or in multimode resonant cavities.

5 As already said, the operating frequency of all these devices within the scopes of the present invention is in the range of UHF and SHF frequencies, i.e. in the range of from 300 MHz to 30 GHz. Generally, it will be possible and particularly convenient to use devices operating at a fixed frequency, i.e. devices fed by one or several microwave generators emitting a predetermined and constant frequency within the aforesaid limits,
10 or more properly (as well known to those skilled in the art) to use one or more generators of electromagnetic waves of a frequency comprised within a narrow range of variability around the aforesaid "constant frequency" value. For reasons of technical and economical convenience, the practical embodiment of the present invention will be particularly advantageous by working in one of the frequency ranges allocated by
15 national and international official authorities for free power uses in industrial, scientific and medical fields, or "ISM frequencies". Said ISM frequencies are: 896 ± 10 MHz in the United Kingdom, 915 ± 13 MHz in the USA, 2450 ± 50 MHz worldwide, 5800 ± 75 MHz and 24125 ± 125 MHz in most countries.

As known to the experts, a large variety of generators, for both laboratory and
20 industrial uses, are available on the market, and the commonest of them are those known as "magnetrons", operating at each frequency among the aforesaid ones, having a different output power (fixed, or continuously variable at will), which can be adapted to the different needs of the specific device and process. For the purposes of the present invention, it is possible to use, in a particularly advantageous way, the ISM frequency of
25 2450 ± 50 MHz, i.e. the frequency most commonly used worldwide for the widest variety of applications. Still as it is known, it is also possible to use more complex and versatile generators, such as the variable-frequency ones and typically comprising a signal generator, providing a low-power signal of frequency variable at will within a determined range usually comprised between 0.5 and 20 GHz, and a power amplifier
30 such as a TWT-type tube ("Travelling Wave Tube").

The maximum power of the particular microwave irradiation device can be adjusted through the installation of one or more generators of different power. The total irradiation power onto the semifinished article in the device shall be adjusted, according

to the needs, in different ways, i.e. in particular: a) by continuously varying the power emitted by the generator or generators, in the case continuously-variable power generators have been chosen and installed; b) by emission of pulses of fixed power and proper length while being more or less frequent in time, so that, during time, the average
5 irradiation power is given as desired for the particular purpose, in the case generators having a constant emission power have been chosen and installed.

Within the scope of the present invention, the implementation of step (iii) of hot and fast post-processing under microwave irradiation can, as already explained, be carried out continuously or discontinuously. The microwave irradiation device will be
10 selected among the aforementioned ones also to the purpose of making it suitable, in a better way, for the particular needs of the discontinuous or continuous process being involved. Discontinuous processes can preferentially be carried out by using closed-chamber irradiation devices of the "multimode resonant cavity" type. For continuous
15 processes, all the devices mentioned above can be used and modified for their conversion to "tunnel" systems, i.e. systems endowed with pairs of inlet and outlet openings of the semifinished article, portion or component thereof, or also of the semifinished article solely heated in the case the hot machining stage of the process begins inside the microwave heating device and ends outside it, or it is performed entirely downstream and outside said heating device.

20 As already reported, all the microwave irradiation devices can optionally be endowed with an appropriate auxiliary conventional heating or thermostating source, working by blowing, or by a forced circulation of, air, other gases or vapors. Such auxiliary heating or thermostating devices will conveniently be used to minimize heat losses from the surfaces of the semifinished articles which have quickly been microwave
25 heated and/or to minimize the inner temperature inhomogeneities, as said above. According to a plant configuration being in use from decades in the vulcanization of extruded rubber profiles under microwave irradiation joined to hot air or combustion gases, tunnel ovens having cross section, length and internal volume diversified according to the particular needs, can conveniently be used for the purposes of the
30 present invention, said ovens being formed by either a single chamber of multimode microwave resonant cavity type, or a series of separate chambers, still of multimode resonant cavity type, connected with or close to each other.

The choice of the suitable type of applicator is linked to different factors, mainly to

the particular kind of post-processing and to the features of the semifinished article to be treated. The overall power and the volumetric density of irradiation power in the device must be chosen case by case and properly, depending on the heating rate being desired, the starting temperature and the temperature required for the post-processing of the particular semifinished article, the mass or volume of polymeric material to be heated, as well as the inherent heatability of the polymeric composition of the present invention being used in the manufacture of the semifinished article. Said polymeric composition can be varied at will, within the aforementioned concentration ranges of its various components, not just to the purpose of adapting its physico-mechanical properties to the final application of the article, part or finished component thereof and its rheological properties to the manufacturing process of the semifinished article, but also aimed at adjusting, in the desired way, its intrinsic microwave heatability. With the same inherent heatability of the composition, its actual heating rate in the device shall progressively be increased by increasing the volumetric density of microwave irradiation power.

The adjustment of the intrinsic heatability of the polymeric compositions through appropriate dosage variations of the relevant components, allows for varying in the desired way the heating rate of the semifinished article with the same level of total power and volumetric density of power of the microwave irradiation device. Above all, the adjustment of the intrinsic heatability of the polymeric compositions represents a particularly advantageous way to optimize the overall processing conditions when used in combination with the adjustment of the irradiation power applied. More particularly and in the most advantageous and effective way, the intrinsic microwave heatability of the polyolefin compositions of the present invention can be increased or lowered by increasing or diminishing, respectively, the whole weight percentage of the "B + C + D" system of components, the whole weight percentage of the "B + C" and "C + D" systems, or yet the weight percentage of the individual "B", "C" or "D" components. By keeping constant the microwave heatability of a certain kind of composition, the weight percentage of metal powders therein (component "B") can be increased or diminished significantly, even of several units of percent, by increasing or diminishing, respectively and in the proper way, the weight percentage of the "C + D" system of components or of the sole "C" component, or yet of the "C" and "D" components independently from each other.

In all cases, the efficiency of the "B + C + D" system of components, as a means to induce the microwave heatability of polyolefin materials according to the present invention, is particularly and advantageously high. Said efficiency is in fact such that it allows surprisingly high heating rates of the compositions under the influence of this kind of electromagnetic irradiation, even under low overall irradiation power levels and/or low volumetric densities of microwave irradiation power, irradiation conditions which can heat very poorly, or unsatisfactorily at all for the fast post-processing operations said above, the polyolefin compositions of the previous art containing an identical weight percentage of the same metal powder or mixture of metal powders. This is also well shown by the practical examples of the present invention. As still shown through the practical examples reported in following, both the components "C" and "D" taken separately and the "C + D" system of components are conversely per se completely devoid of capabilities to promote any microwave heatability of the polyolefin polymers whereinto they are dispersed, even though they are present in particularly high weight percentages, in the absence of metal powders. In other words, the "C + D" system of components emphasizes at remarkable and surprising extents the microwave heatability proper to the compositions made of polyolefin polymers and metal powders, or metal powders in combination with additives or auxiliaries of the known art and selected among those previously cited.

In this way, the present invention allows for implementing thermoplastic polyolefin compositions endowed with a microwave heatability comparable to that of similar compositions of the known art containing percentages of metal powders 30% higher at least, and thus endowed with superior physico-mechanical properties (particularly, toughness) in the solid state, lower density (thanks to the lower amount of high-density metal powders) and much better attitudes to be colored with pigments or dyes (yet thanks to the lower portion of metal powders), as well as lower melt-viscosity (and thus having an easier processability) by virtue of the lower volumetric fraction of dispersed, solid metal particles. As already reported, the heatability of the present compositions can be varied within very broad limits by a proper selection of components (and particularly components "B", "C" and "D", and the combinations thereof), or their relevant weight percentages. The actual heating rate of the same composition under microwave irradiation depends significantly on the volumetric density of irradiation power applied in the particular device being used case by case, as well as, yet and in a

more complex way being known to the experts in the field, on the impedance difference between the irradiated article and the irradiation device (i.e. on the “degree of electromagnetic matching” between article and device). For example, according to a particularly preferred embodiment of the invention, the compositions of the present invention, having been converted into small objects of different shape, can exhibit excellent heating rates in the range of from 2 to 5°C/second even under a modest volumetric density of irradiation power of about 48 mW/cm³ in conventional microwave ovens in air at room temperature. Even under so mild treatment conditions, said heating rates are sufficient to reach, starting from room temperature, temperatures of 80-130°C (more than adequate for most hot post-processing operations on the polyolefin materials of the present invention) within times not longer than 40 seconds, and generally even shorter.

The strong microwave heatability proper to the present compositions even though containing modest amounts of metal powders, thanks to the effects of the already described “C + D” system of components of organic chemical nature, implies a further and important advantage of the compositions of the present invention over those of the previous art. Said advantage consists of the possibility of implementing compositions which can be heated with extremely high rates (for instance, of the order of ten degrees centigrade per second, and even higher) and without any electric surface discharges under high volumetric densities of microwave irradiation power, irradiation conditions under which the compositions of the known art, comparably heatable thanks to higher amounts of metal powders, on the contrary and easily give place to this kind of phenomena, particularly dangerous (for the ignition of fires) and damaging the article being heated.

According to what reported above and to an alternative embodiment of the processes of the present invention, it is possible and advantageous to carry out the processing step (iii) by using microwave irradiation (optionally assisted, as already said, by a stream of air, other gases and/or vapors) in conjunction with simultaneous infrared irradiation, the latter having specific heating effects over the surface layers of the semifinished article made of polymeric material being processed. Said simultaneous microwave and infrared electromagnetic irradiation of articles made of the compositions of the present invention is particularly advantageous in the following two cases:

a) in the post-processing operations of the (iii) step, carried out in microwave

irradiation devices in air at room temperature in the absence of hot air, gases and/or vapors as supplementary heat sources for the surface heating of the articles being treated (i.e. in devices of limited dimensions and implying much lower, overall energy consumptions);

- 5 b) in the post-processing operations under microwave irradiation (particularly if carried out in air at room temperature) concerning semifinished articles characterized by high surface-to-volume ratios (such as sheets, slabs, straps, ribbons, fibers and fiber strings, nets and grids, and so on).

10 In the second case, in fact, the heat dissipation rate per unit volume of the semifinished article by infrared surface irradiation directly outwards, and by convective heat abstraction from surfaces by the surrounding atmosphere, is particularly intense because of the large surface area of the semifinished article being exposed externally with respect to the volume of the polymeric material forming said article. The infrared irradiation of the surfaces of the semifinished articles, associated with the microwave
15 one applied to their entire volume, thus allows the attenuation or minimization of the spontaneous inferiority of the surface temperature of the semifinished articles, having modest thicknesses, with respect to the temperature of their internal portions, nicely microwave-heatable. As known to those skilled in the art, such temperature uniformity, or minimized temperature inhomogeneity, results into an easier and faster hot forming
20 of the articles, as well as into finished articles, parts or components made of plastic material having a more homogeneous internal microstructure, free from or containing lower internal stresses, and therefore endowed with a higher brittle-fracture resistance, better time stability, and more consistent mechanical and thermo-mechanical properties.

25 As already said, the polyolefin compositions of the present invention include the "C + D" system of components endowed with nice infrared absorption capabilities over the wavelength spectrum of from 5.5 to 13 μm (as shown in the following practical examples). This, associated with the infrared absorption contribution proper to the polyolefin material being the component "A" at frequencies around 3.5 μm and with the low volumetric fractions of infrared-reflecting metal powders which characterize the
30 present compositions versus those containing metal powders of the previous art, makes the compositions of the present invention advantageously well-heatable on their surfaces by infrared irradiation, with a particular efficiency by such radiation having a wavelength in the range of from 3 to 25 μm , and even more efficiently by radiation with

wavelength being comprised within the intervals of from 3.2 to 3.8 μm and 5.5 to 15 μm .

As known to the experts in the field, infrared radiators emit, at each temperature of themselves, a continuous infrared spectrum whose wavelength of maximum emission intensity, linearly decreasing as their own temperature raises, can be calculated with a good approximation by the known equation: $\lambda_{\text{max}} (\mu\text{m}) T(^{\circ}\text{K}) = 2898 (\mu\text{m } ^{\circ}\text{K})$, wherein λ_{max} is said wavelength of maximum intensity, and T is the absolute temperature of the radiator. A description of main theoretical and practical aspects regarding radiant heat transmission is reported, e.g., in the publication "Heat transmission by radiation", by J.G. Knudsen et al., in the volume "Perry's Chemical Engineers' Handbook" 6th edn., McGraw-Hill, New York, 1984, pages 10-52 – 10-68, the contents of which are herein included as reference.

By virtue of the wide wavelength range covered by the continuous emission spectrum of every infrared radiator, any infrared irradiation device can efficiently be used in combination with the microwave irradiation device selected for the purposes of the present invention, i.e. for the simultaneous heating of the surfaces and the inner parts of articles made of the polyolefin compositions of the present invention. For the present purposes, said infrared radiators must be installed inside the microwave irradiation device, and in such a way that they may neither shield or interfere with the microwave irradiation within the same device, nor generate electric discharges under the influence of the microwave electromagnetic field.

As known, a variety of useable infrared radiators and suitable technical solutions for their installation inside microwave irradiation devices are available. Examples of infrared radiators suitable in accordance with the present invention, but not by way of limiting the same, are armored electric resistors (electrically connected to the inner metal walls of the microwave irradiation device) and metal or silicon carbide electric resistors protected by metal grids. Suitable infrared radiators for the purposes of the present invention are also static bodies made of inert materials being per se microwave-heatable and efficiently heated by the same electromagnetic field being used for the heating of the semifinished article, and simultaneously with the microwave heating of the semifinished article itself. Radiators of such a kind can be made, for instance, of glass, ceramics, porcelain, glass-ceramics, and so on. Radiators of all these types can be placed more or less far from the semifinished article, as well as spatially placed and/or shaped in

different ways in order to irradiate homogeneously the semifinished article surfaces, depending on the shapes thereof. In particular, planar semi-finished articles, such as slabs, sheets, nets and grids, can be homogeneously irradiated by infrared radiation by using radiators, of the aforementioned types, being placed both above and beneath the
5 plane of the semifinished article itself.

According to the aforesaid expression of the wavelength of maximum emission intensity of infrared radiators as a function of their temperature, the temperature of a radiator exploiting at best the energy absorption capabilities of the polyolefin material surfaces is near 550°C. A radiator working at a moderate temperature comprised
10 between 100 and 250°C shows conversely the highest emission intensity in the wavelength range of 5.5-8 μm , corresponding to a spectral range of good absorbance by the "C + D" system of components of the compositions of the present invention. In accordance with such indications, a further and advantageous embodiment of the infrared irradiation treatment of the surfaces of semifinished articles made of the
15 compositions of the present invention consists in the use of infrared radiators kept at modest temperatures, and preferentially within the range of from 100 to 250°C. Said modest temperatures advantageously allow for employing, as infrared radiators, static bodies placed in the proximity of the semifinished article, or also the internal metal walls themselves of the microwave irradiation device (especially if surface-treated to improve
20 their own infrared emissivity), heated by the air or gas flow optionally useable in combination with microwave irradiation, as already said.

The hot post-processing operations being an integral part of step (iii) of the processes being an object of the present invention, are preferentially carried out inside the microwave irradiation device and simultaneously with the microwave heating of the
25 semifinished article. Alternatively, the same post-processing operations can be initiated inside the microwave irradiation device and completed as the semi-finished article (still hot) leaves it, or they can also be carried out entirely outside the same microwave irradiation device onto the semifinished article just heated up to the desired post-processing temperature, or even to a higher temperature.

30 The post-processing method can be very different case by case, depending on the desired shape, aspect ratio and dimensional modifications of the articles to be fabricated, as well as of the semifinished article shape and/or size. In all cases, and already reported, said post-processing methods imply the application of a mechanical stress or a

combination of different mechanical stresses applied simultaneously, or subsequent to each other in time or space, to the semifinished article heated. The application of said mechanical stress or combination of mechanical stresses to the semifinished article may be carried out by known and various tools, depending on the type of mechanical stress and shape, aspect ratio or dimensional modification to be imparted to the semifinished article. Non-limiting examples of said tools are the following ones: pneumatic or mechanical clamps, grips and forceps, friction rolls, pistons, punches, planar plates, molds and counter-molds, conical or cylindroconical drawing dies, pressure rolls having a smooth or grooved surface, or also bearing various figures in relief or intaglio figures, and many others.

In the discontinuous processes, both the fast microwave heating (or the simultaneous microwave and infrared irradiation heating) and the application of mechanical stresses to the semifinished article are carried out discontinuously.

Non-limiting examples of such accelerated discontinuous processes, according to the present invention, are the following ones:

- a) bending of extruded pipes, and pieces of extruded and sectioned pipes;
- b) cylindroconical necking or flaring of terminal segments of pieces of extruded pipes (formation of bell and spigot joints);
- c) manufacture of open containers of various shape by die forming of sheets or slabs having uniform thickness, or locally differentiated thickness zone by zone, pre-perforated sheets or slabs, and so on;
- d) manufacture of shaped panels having various and even involved shapes by thermoforming of sheets or slabs of uniform thickness or having local thickness differences.

In the continuous processes of the present invention, both the fast microwave heating (or the simultaneous microwave and infrared irradiation heating) and the application of mechanical stresses to the semifinished article are carried out continuously. Representative, but non-limiting examples of said accelerated continuous processes on continuous semifinished articles, according to the present invention, are the following ones:

- a) conversion of sheets or slabs of uniform thickness into continuous or discontinuous sheets or slabs having locally differentiated thickness according to predetermined patterns;

- b) conversion of continuous straps or strips into profiles having a different open cross section (L, U, V, Z-shaped profiles, and so on);
- c) uni- or bi-axial stretching of thin sheets or slabs;
- d) axial stretching of extruded strips, rods or thin tubes having a small cross section,
5 yarns, filaments or fiber strings;
- e) forming nets, grids, geo-nets or geo-grids, and other various network structures having a planar conformation, by stretching, being either uni-axial in the flow direction along the heating device or bi-axial in this direction and orthogonal to it, of extruded slabs or sheets, or yet initially extruded and then calendered slabs or
10 sheets, bearing predetermined spatial patterns of die-cut and variously shaped holes, or also of punched depressions (examples of fabrication of such products by conventional methods are those disclosed in the already-cited US patents 4,303,714, 4,374,798, 4,574,100, 4,590,029, 4,618,385, 4,652,409, 4,743,486, 5,419,659, and 6,423,394);
- 15 f) forming various network structures, having a planar conformation as the aforementioned ones, or like them but endowed with protrusions orthogonal to the plane, or still also tri-dimensional, by uni- or bi-axial stretching, as defined above, of network “preforms” having an even complex geometry (bearing passing openings, holes, depressions or protrusions, and so on) being directly obtained by
20 continuous dynamic extrusion or co-extrusion processes, or by multiple extrusion combined in a plurality of directions (examples of fabrication of such products by conventional heating methods are disclosed in the aforementioned United Kingdom patent 880,236 and in US patents 4,711,751, 5,667,869, 5,851,089, and 5,891,549).

A further and advantageous use of the thermoplastic polyolefin compositions of the
25 present invention is as welding materials, rapidly fusible under microwave irradiation, for the super-fast joining of objects, parts or components made of different conventional polyolefin materials (as reported, for example, in the aforementioned US patent 5,254,824). For said purposes, the present thermoplastic compositions, previously formed in an appropriate way, are interposed between the faces of the objects, parts or
30 components, made of polyolefin material, to be welded together, and then brought close to or preferentially pressed against each other in order to include “by sandwich” the polyolefin material for microwave welding of the present invention. The present compositions can thus be prepared as small slabs, thin straps, small discs, planar rings,

toroids, thin-walled hollow and open cylinders, and in many other shapes which can fit at best the shapes of the parts to be welded together.

The entire structure consisting of the objects, parts or components to be welded, brought close to or pressed against each other and containing, interposed, the
5 microwave-heatable polyolefin composition, or the sole portion of the structure being involved in the welding treatment, is then submitted to microwave irradiation in one of the irradiation devices described above for a short period of time, generally variable from a few tens of seconds to one minute. The microwave irradiation heats up and rapidly melts the polyolefin composition of the present invention, which, with the same
10 rapidity, hot welds with each other the faces of the objects, parts or components involved. For this use, the microwave-heatable compositions will preferentially be selected from those of the present invention comprising, as the polyolefin component "A", a polyolefin material of the same kind of that of the objects, parts or components to be welded with each other. Non-limiting examples of said articles, parts or components
15 made of polyolefin material, quickly weldable with each other by the present process, are pipes, solid, hollow or open extruded profiles of various shape, slabs and other planar items, and many others. For the present, aforementioned use, the polyolefin compositions of the present invention display, with respect to those of the previous art, the considerable advantage of containing a much lower volume percentage of additives acting as "susceptors" of microwave heatability (in the present compositions, the "B + C
20 + D" system of components), and thus of allowing the hot junction by a welding material having a composition much closer to that of the material of the objects, parts or components to be welded with each other. Therefore, this allows for obtaining junctions much more homogeneous and stronger than those attainable through the compositions of
25 the known art.

A still further and advantageous use of the present compositions is forming semifinished articles having a composite polymeric structure, comprising parts or components made of a rapidly microwave-heatable polyolefin material according to the present invention, and parts or components made of one or several conventional, non-
30 microwave heatable, polyolefin materials, parts or components, having a different composition, being in contact, welded or variously interpenetrated with one another. Said semifinished articles having a composite polymeric structure can be made, preferentially but in a non-limiting way, by discontinuous forming processes, such as co-

injection molding of the different materials, or by continuous, static or dynamic, co-extrusion of the different materials to afford a single continuous semifinished article having a planar or non-planar network structure, or also being a bi- or tri-dimensional "pre-form" like the aforementioned ones.

5 In said semifinished articles having a composite polymeric structure, the parts or components made of a polyolefin material with a composition according to the present invention can selectively and rapidly be heated under microwave irradiation, while leaving cold or just slightly heated, on the contrary, the parts or components made of conventional, non-microwave heatable, polyolefin material. Under microwave
10 irradiation, or under simultaneous microwave and infrared irradiation, it is thus possible to selectively subject to rapid hot forming, or to fast shape and/or aspect ratio variations, only those parts or components of the semifinished articles being made of a thermoplastic polyolefin material prepared by the compositions of the present invention. Also in this usage mode, the compositions of the present invention are particularly
15 advantageous over those of the known art, by virtue of their much lower volume proportion of additives acting as "susceptors" of microwave heatability. As a matter of fact, when compared to the microwave-heatable polyolefin compositions of the known art, the present compositions are materials much more inter-compatible with and adhesive onto conventional polyolefin materials (free from additives acting as
20 "susceptors" of microwave heatability) in the critical joining areas between different materials within the semifinished article and the finished article having a composite polymeric structure.

The thermoplastic polyolefin compositions disclosed above, the preparation and processing methods thereof, being the object of the present invention, as well as the
25 relevant advantages, will be outlined in detail through the following examples, which, however, are hereinafter reported only for illustrative purposes and not by way of limitation of the whole scope of the present invention.

EXAMPLES

In the following examples, the preparations of the polymeric compositions of the
30 present invention were carried out by using a laboratory mixing device for molten polymers Haake PolyLab System. In particular, the preparations were performed in a Haake Rheomix mixer (driven by the Haake Rheocord unit) equipped with a mixing chamber having a total volume of 63 cm³ and conventional rotors for plastic materials,

by charging from time to time an overall amount of 50-55 g of mixtures of the components pertaining to each composition. All the samples were prepared with a rotation speed of the rotors of 35 r.p.m and by using a total mixing time of 10 minutes. The temperature setting of the mixing chamber was varied in the following way,
5 depending on the composition type: 160°C for the LDPE low density polyethylene-based compositions; 180°C for the HDPE high density polyethylene-based compositions; and 200°C for the polypropylene-based ones.

The warm and plastic polymeric compositions recovered from time to time at the opening of the mixing chamber were immediately converted into slabs having a
10 thickness of about 2 mm by a hot-plate press, slabs which were then cut into small cubic pieces after cooling.

For the microwave heating tests on the various polymeric compositions described in the following examples, cylindrical test pieces were prepared having both diameter and height of 3.8 cm. Said test pieces were obtained by slow hot compression of cubic
15 granules in a heated cylindrical metallic mold. Said test pieces will be identified in the following examples as "cylindrical test pieces".

For the internal temperature measurements of the material, two cylindrical holes, with a 1.55 mm diameter and 19 mm-deep, were drilled on the plane surfaces of each test piece, one along the test piece axis and the other, parallel to the first one, at half the
20 radius of the cylindrical test piece, while the surface temperature measurements were always performed in the middle of one of plane surfaces.

The internal temperature measurements of the aforementioned test pieces were performed by using a stylus-type NiCr-Ni, "class 1", thermocouple with a 1.5 mm diameter (having a stabilization time of 2 seconds to $\pm 0.2^\circ\text{C}$ readings), while for the
25 surface measurements again a NiCr-Ni, "class 2", thermocouple of ribbon type for surfaces (having a stabilization time < 3 seconds to $\pm 0.2^\circ\text{C}$ readings) was used, said thermocouples being connected to a Testo GmbH, mod. 945, digital thermometer.

The heating tests on said test pieces under microwave irradiation, and simultaneous infrared and microwave irradiation, were carried out in a combined Electrolux Heat
30 Wave System oven, mod. EMM 1871, internally ventilated and working at the ISM frequency of 2450 MHz, with an effective microwave irradiation power variable from 0 to 800 W, modified by equipping it with a lateral port protected by a cylindrical waveguide segment, made of aluminum, having a 32 mm diameter, and by installing one

of the two 550 W-each infrared radiators in a front position, in order to guarantee a homogeneous infrared irradiation from the ceiling of the chamber.

All the microwave heating tests were performed, at the constant irradiation power of 800 W, by maintaining, one at a time, a cylindrical test piece of the aforesaid type on the rotating plate of the oven for different, exactly measured time intervals, said test piece being vertically placed in a cylindrical Teflon container (having an internal diameter and height of 5 cm), in its turn placed over a 10 mm-thick Teflon plate. The simultaneous infrared and microwave heating tests were carried out in the same way (always under a microwave irradiation power of 800 W), after having brought the infrared radiators to their measured regime temperature of 500-550°C, and by keeping the upper plane face of the test piece at a distance of about 6 cm from the infrared radiators on the ceiling of the oven.

The measurements of internal and surface temperature values reached by the test pieces after different pre-selected irradiation time intervals were performed by switching off and opening the oven at the end of the time period and by placing manually and quickly the stylus-type temperature probe into one of the appropriate test piece holes through the lateral port of the oven, or by applying in the same way the surface temperature probe onto the test piece. The overall delay of temperature readings with such procedure (positioning time + stabilisation time of temperature readings) is comprised in the range of from 5 to 6 seconds. For such reason, the temperature values reported in the various examples actually are slightly underestimated values (on average, by 2°C for the internal temperature measurements, and by about 4°C for the surface ones) with respect to the values really reached time by time by the test pieces. After every single exposure to irradiation, and prior to the subsequent test, the test pieces were reconditioned 30 minutes under a forced air stream at 23°C, this temperature being the initial one for all the heating tests. In the different practical examples, the temperature values reached internally and at the surface by the various compositions, after different electromagnetic irradiation times starting from 23°C, are identified as hereinafter reported. All the temperature values reported in the following examples are expressed in degrees centigrade.

- internal temperature at the center of the test pieces: "T₁",
- internal temperature of the annular zone at half radius and half height of the test pieces: "T₂",

- surface temperature in the middle of the upper plane face of the test pieces: “ T_s ”.

The concentrations of the components of the different compositions cited in the following examples are always expressed as weight percentages.

Example 1 and Comparative Examples C1 and C2

5 In accordance with the procedure described above, a sample was prepared of the polyolefin composition from the components hereinafter listed with the relevant weight percentages (Composition E1).

- granular LDPE low density polyethylene [melting point = 118°C, density = 0.933 g/cm³, and Melt Flow Index (190°C/2.16 kg) = 3.5 g/10 min]: 81.00%;
- 10 - aluminum powder, with lamellar particles (particle size range = 1 to 72 µm, average particle size = 25 ± 0.5 µm): 7.00%;
- tribenzylamine, finely powdered: 2.00%;
- ethylene-acrylic acid copolymer (5% by weight of acrylic acid) [Brookfield viscosity (145°C) = 575 cps]: 10.00%.

15 The thin plane slab of the composition, obtained as above reported by hot pressing the molten product recovered from the mixer, showed a light grey color, with a slightly metallic gloss.

For comparative purposes, samples of the two compositions described below were prepared with the same procedure.

20 Comparative Composition C1:

- the same LDPE polyethylene of the Composition E1 described above: 88.00%;
- tribenzylamine: 2.00%;
- the same ethylene-acrylic acid copolymer of the Composition E1 described above: 10.00%.

25 Comparative Composition C2:

- the same, aforementioned LDPE polyethylene: 92.50%;
- the same aluminum powder used in the Composition E1 described above: 7.00%;
- commercial, stearic acid powder: 0.50%.

30 A cylindrical test piece of each one of the aforesaid compositions E1, C1 and C2, prepared according to the procedure described above, were subjected to a microwave irradiation treatment for three different time periods of 10, 20 and 30 seconds, with the aforesaid procedure of treatment and measurement of the temperatures reached by the material in the different test piece positions. Such temperature values reached by the

different compositions after the three different time intervals are reported in Table I.

Table I

time (seconds)	Composition						
	E1			C1	C2		
	T ₁	T ₂	T _s	T ₁	T ₁	T ₂	T _{1s}
10	70.4	59.7	37.8	24.6	54.0		
20	105.5	80.8	54.2	25.9	87.8	75.8	47.7
30	122.7*	102.6	73.1	27.1	98.4		

* material melting

The temperature values shown in Table I for the three different compositions clearly show: a) the negligible capabilities of the system of components of the present invention (2% benzylamine + 10% ethylene-acrylic acid copolymer) to impart per se a microwave heatability to the polyolefin material (Composition C1); b) the remarkable capabilities of the system of components of the present invention (tribenzylamine + ethylene-acrylic acid copolymer) to enhance the microwave heatability of the polyolefin filled with the same kind and percentage of aluminum powder (comparison between Composition E1 and Comparative Composition C2); c) the spontaneous and systematic temperature inhomogeneity of the various materials occurring upon the microwave heating treatment, for both the test pieces of the Composition E1 of the present invention and the Comparative Composition C2.

Example 2

The same test piece of Composition E1 of the previous example was subjected to a simultaneous microwave and infrared irradiation treatment in accordance with the general testing procedure described above, for two different periods of 20 and 30 seconds.

The different temperature values reached by the material through this combined, 20 and 30 second-long irradiation treatment were compared with those measured in Example 1 after 20 and 30 seconds of microwave irradiation only, as shown in Table II.

The diagram of the enclosed drawing shows the portion over the 4-13 μm frequency range of the reflected infrared absorption spectrum given by the surface of the

Composition C1 of the previous example, containing the same components (except for the metal powder) of the Composition E1, being the object of the present example. According to what previously said, such spectrum exemplifies the energy absorption capabilities of the polyolefin composition of the present invention in the particular frequency range of infrared radiation to which neat polyolefin polymers are conversely known to be almost perfectly indifferent.

Table II

Composition E1						
time (seconds)	microwave			microwave + infrared		
	T ₁	T ₂	T _s	T ₁	T ₂	T _s
20	105.5	80.8	54.2	106.2	83.2	78.0
30	122.7	102.6	73.1	123.9	108.3	110.3

As exposed in Table II, the comparison among the temperature levels reached in the sample by microwave irradiation only and by simultaneous microwave and infrared irradiation, respectively, shows the capabilities of the Composition E1 according to the present invention to undergo heating as much internally with a surprising rapidity (with an average heating rate in the core of the test piece of 3.2 °C/sec under the relatively mild experimental conditions adopted), as with a particular homogeneity of the inner and surface temperature (in consideration of the remarkable thickness of the test piece submitted to testing) through the combined electromagnetic irradiation treatment being an object of the present invention.

Example 3 and Comparative Example C3

In accordance with the same general procedure previously disclosed, a sample of a polypropylene-based polyolefin composition was prepared comprising the components listed below (Composition E2).

- granular, extrusion-grade polypropylene homopolymer [melting point = 163°C, density = 0.905 g/cm³, and Melt Flow Index (230°C/2.16 kg) = 1.9 g/10 min]: 83.70%;
- granular, low molecular weight polypropylene homopolymer [Brookfield viscosity (190°C) = 6.0 poise]: 5.00%;

- the same aluminum powder used in Example 1: 7.00%;
- finely powdered triphenylphosphine: 3.80%;
- dodecenylsuccinic acid: 0.20%;
- pure stearic acid powder: 0.30%.

5 For the sake of comparison, a sample of Comparative Composition C3, hereinafter reported, was prepared in the same way.

- the same extrusion-grade polypropylene used in Composition E2: 87.50%;
- the same low molecular weight polypropylene used in Composition E2: 5.00%;
- the same aluminum powder used in Composition E2: 7.00%;
- 10 - pure stearic acid powder: 0.50%.

Table III

Composition						
time (seconds)	E2			C3		
	T ₁	T ₂	T _s	T ₁	T ₂	T _{1s}
10	61.5			55.6		
20	96.4	79.3	55.1	89.7	75.9	47.8
30	135.8	127.9	77.6	104.7		56.6
40	158.5			127.1		

A cylindrical test piece of Composition E2 and one of the Comparative one C3 were subjected to irradiation treatments for four different time intervals of 10, 20, 30 and 40 seconds, with measurement of the temperature values reached time by time in the different positions of the test pieces themselves, according to the general procedure previously described and used in Example 1. The results of such tests, as reported in Table III, show the enhanced microwave heatability of the Composition E2 of the present invention with respect to the Comparative Composition C3, containing the same percentage of the same metal powder. By referring to the T₁ temperature values reached in the core of the test piece after the same irradiation time, the average gain of microwave heatability of Composition E2 with respect to the Comparative Composition C3 was about 23% over the entire interval of treatment times from 10 to 40 seconds, while the net heatability gain after the longer irradiation times of 30 and 40 seconds was even higher, and of about 30-38%.

Example 4

For the heatability tests of the present example, a new sample and a new cylindrical test piece of the same Composition E2 of the previous example were prepared in accordance with the already cited procedure.

Table IV

Composition E2						
time (seconds)	microwave			microwave + infrared		
	T ₁	T ₂	T _s	T ₁	T ₂	T _s
20	95.8	78.9	55.5	96.1	81.3	77.7
30	133.4	125.7	76.9	134.0	129.5	114.9

5 The test piece was at first subjected to two microwave irradiation tests of 20 and 30 seconds, and subsequently to a couple of combined microwave and infrared irradiation tests, still 20 and 30 second-long, with measurement of the internal T₁ and T₂ temperatures, and the T_s surface temperature, reached at the end of the two different treatment times. The data relevant to such tests are reported in Table IV. Similarly to
10 what shown in Example 2, the data of Table IV point out also in this case the possibility of combining an excellent heating rate of the plastic material of the composition of the invention with a nice balance among the internal and surface temperatures of the object irradiated.

Examples 5 and 6, and Comparative Example C4

15 According to the same general procedure of previous examples, samples and relevant test pieces of the two Compositions E3 and E4, based on high density polyethylene, were prepared as hereinafter indicated.

Composition E3.

- granular, HDPE high density polyethylene [melting point = 130-133°C, density =
20 0.949 g/cm³, and Melt Flow Index (190°C/2.16 kg) = 3 g/10 min]: 86.30%;
- aluminum powder, being a mixture of dendritic-acicular and small cavernous particles (having a particle size distribution spanning the range of from 0.5 to 155 μm, and an average particle size of 52 ± 1 μm): 7.00%;
- finely ground tribenzylamine: 3.00%;

- finely ground triphenylphosphine: 0.90%;
- the same ethylene-acrylic acid copolymer used in Composition E1 of Example 1: 2.80%.

Composition E4.

- 5
- the same HDPE polyethylene of Composition E3: 88.55%;
 - the same aluminum powder of Composition E3: 7.00%;
 - tribenzylamine: 3.90%;
 - pure stearic acid powder: 0.55%.

For the sake of comparison, a sample and cylindrical test piece of the Comparative Composition C4 were prepared with the hereinafter listed components:

- 10
- the same HDPE polyethylene of Compositions E3 and E4: 92.45%;
 - the same aluminum powder of Compositions E3 and E4: 7.00%;
 - pure stearic acid powder: 0.55%.

The results of the microwave heating tests on the test pieces of the two Compositions E3 and E4 are reported in Table V.

15

Through the present examples, it is further demonstrated the superior microwave heatability of the compositions of the present invention with respect to the conventional ones, filled with the same weight percentage of the same metal powder.

Table V

Composition									
time (seconds)	E3			E4			C4		
	T ₁	T ₂	T _s	T ₁	T ₂	T _s	T ₁	T ₂	T _s
10	80.6			82.3			68.2		
20	104.5	95.7	60.6	110.4	94.9	62.0	97.2	85.7	51.5
30	118.0			123.4			106.5		

In particular, Compositions E3 and E4 display an especially-emphasized microwave heatability (i.e. being able to undergo heating in the core of test pieces with a rate 30% higher than the corresponding Comparative Composition C4) precisely and advantageously during the first heating step starting from room temperature (in this particular case, over the initial 10 seconds of irradiation).

20

Example 7

In a one-liter, three-necked spherical glass flask, fitted with a double surface reflux condenser, dropping funnel, inlet tube of pure and dry argon, and ovoidal magnetic stirring bar, an ethereal solution of *para*-tolylmagnesium bromide was prepared according to a known synthetic procedure, by using 9.7 g of magnesium turnings, 68.4 g of *para*-bromotoluene and 350 ml of anhydrous ethyl ether. Always under a very slow stream of dry argon and with vigorous magnetic stirring, a solution of 90.7 g of chlorodiphenylphosphine in 100 ml of anhydrous ether was added dropwise to said solution in the flask, at such a rate to maintain spontaneous boiling of the mixture, over a period of about 40 minutes. The mixture was then heated and maintained boiling under reflux, always under rapid magnetic stirring, for about three hours, cooled and then poured under stirring into about 500 ml of cold water. The ethereal solution was separated in a separatory funnel, and washed four times with water, once with a 0.5 N sodium hydroxide solution, further four times with water, dried over anhydrous magnesium sulfate, and then evaporated in a rotary evaporator, initially at atmospheric pressure and finally under reduced pressure. The crystalline product resulting from evaporation, having a just pale yellow color and consisting of 90.5 g of raw diphenyl-*para*-tolylphosphine (with a melting point in the range of from 60 to 66°C) was used, after grinding, in the preparation of the polyolefin Composition E5, made of the components listed in the following.

- the same granular HDPE high density polyethylene used in Compositions E3 and E4 of Examples 5 and 6: 86.46%;
- the same aluminum powder used in the preparation of Compositions E3 and E4 of Examples 5 and 6: 6.00%;
- extra-fine brass powder, consisting of a mixture of lamellar and acicular particles (with a particle size distribution in the range of from 0.6 to 34 μm , and an average particle size of $8 \pm 0.5 \mu\text{m}$): 4.00%;
- finely powdered diphenyl-*para*-tolylphosphine, prepared as described above: 3.00%;

Table VI

Composition E5	
time (seconds)	T ₁
10	61.4
20	74.9
30	107.0

- a mixture of crystalline, higher fatty acids, containing stearic acid (about 60%), palmitic acid (about 30%) and lauric acid (about 10%): 0.54%.

The thin plane slab of the composition, hot-pressed after it was recovered in the molten state from the mixer, displayed a pale golden-grey color, with delicate metallic hues. As shown in Table VI, the excellent microwave heatability of the composition is being pointed out by the central internal temperature values T_1 reached by the relevant cylindrical test piece after irradiation periods of 10, 20 and 30 seconds.

Example 8

By following the same procedure of previous examples, a sample and a cylindrical test piece of Composition E6 were prepared with the following components:

- the same LDPE polyethylene of Composition E1 (Example 1): 91.42%;
- the same aluminum powder of Compositions E3 and E4 (Examples 5 and 6): 5.60%;
- finely powdered tribenzylamine: 2.45%;
- dodecenylsuccinic acid: 0.53%.

The cylindrical test piece of the composition, having a pale grey color with feeble metallic hues, was subjected to three 20, 30 and 40 second-long heating tests under microwave irradiation only, and then to a simultaneous microwave and infrared irradiation test, 20 second-long. The data of Table VII show both the good microwave heatability of the material, and the nice balance of internal and surface temperatures of the test piece attainable through the simultaneous microwave and infrared irradiation process.

Table VII

Composition E6				
time (seconds)	microwave		microwave + infrared	
	T_1	T_s	T_1	T_s
20	70.0			
30	83.9	48.2	85.4	83.0
40	104.8	58.2		

Example 9

By following the same procedure of the chemical synthesis described in Example 7, 69.5 g of raw, crystalline tri-*para*-tolylphosphine (melting over the 140-150°C

temperature interval) were prepared by using the following reactants and solvents: 21.9 g of magnesium turnings; 153.9 g of *para*-bromotoluene; 41.2 g of phosphorus trichloride; 500 ml of anhydrous ethyl ether.

A polyolefin composition (Composition E7) was then prepared, in accordance with the general procedure already disclosed, by using the following components:

- granular, propylene-ethylene block copolymer [having a melting point = 163°C, density = 0.902 g/cm³, and Melt Flow Index (230°C/2.16 kg) = 3 g/10 min]: 82.45%;
- aluminum powder, with lamellar particles (particle size distribution over the range of from 1 to 85 µm, and average particle size of 48 ± 2 µm): 3.00%;
- the same aluminum powder used in Compositions E3 and E4 (Examples 5 and 6): 4.00%;
- commercial triphenylphosphine powder: 2.00%;
- finely ground, tri-*para*-tolylphosphine, prepared as said above: 2.00%;
- super-fine titanium dioxide powder: 2.50%;
- super-fine calcined kaolin: 3.50%;
- pure stearic acid: 0.55%.

The thin plane slab of the composition deriving by hot pressing the molten composition recovered from the mixer, showed a matt surface, having a pale grey color, substantially free from any metallic hues.

The microwave irradiation tests performed onto the cylindrical test piece with three treatment times of 10, 20 and 30 seconds show, as indicated in Table VIII, an excellent heatability of the composition, heatability which is particularly vivid at temperatures above 100°C.

Table VIII

Composition E7		
time (seconds)	T ₁	T _s
10	69.8	54.0
20	108.1	
30	147.0	

CLAIMS

1. Thermoplastic polymeric compositions comprising the following components:
 - A. a thermoplastic polyolefin material;
 - B. a metal powder, or a mixture of different metal powders;
 - 5 C. a tertiary phosphine or amine, or a mixture of two or more different tertiary phosphines and/or amines, having general formula $ZY_1Y_2Y_3$, wherein Z is a phosphorus or nitrogen atom and Y_1 , Y_2 and Y_3 , equal to or different from each other, are C_6-C_{18} aryl, C_7-C_{36} alkylaryl, C_7-C_{36} alkoxyaryl radicals, mixed C_8-C_{36} alkyl-alkoxy-aryl radicals, C_9-C_{24} cycloalkylaryl radicals, mono-, bi-, or
10 triarylmethyl radicals wherein the aryl radical contains from 6 to 18 carbon atoms, mono-, bi- or trialkylarylmethyl radicals wherein the alkylaryl group contains from 7 to 36 carbon atoms, or mono-, bi- or tricycloalkylarylmethyl radicals wherein the cycloalkylaryl group contains from 9 to 24 carbon atoms;
 - D. an organic or inorganic mono-, di- or polybasic protic acid, or a mixture of two or
15 more different organic and/or inorganic mono-, di- or polybasic protic acids.
2. Compositions according to claim 1, wherein the component "D" is absent.
3. Compositions according to claim 1 or 2, wherein the thermoplastic polyolefin material, identified as the component "A", consists of a polyolefin-type thermoplastic polymer.
- 20 4. Compositions according to any of the preceding claims, wherein the polyolefin-type thermoplastic polymer being the polyolefin material indicated as the component "A", is selected from the group consisting of the homopolymers of the α -olefins containing from 2 to 18 carbon atoms, the copolymers and terpolymers of two or three of said α -olefins, respectively, the copolymers of an α -olefin, as described above, with an
25 unsaturated comonomer of different nature, or yet the terpolymers of one or two of said different α -olefins with two unsaturated comonomers or one unsaturated comonomer of different nature, respectively.
5. Compositions according to claim 4, wherein the polyolefin-type thermoplastic polymer is selected from the group consisting of the homopolymers of ethylene, such as
30 low density polyethylene (LDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), ultra-high molecular weight polyethylene (UHMWPE), as well as the copolymers and terpolymers of ethylene with minor weight portions of α -olefins having a number of carbon atoms comprised in the range of from 3 and 18, such as

linear low density polyethylene (LLDPE), very-low density polyethylene (VLDPE) and ultra-low density polyethylene (ULDPE).

6. Compositions according to claim 4, wherein the polyolefin-type thermoplastic polymer is selected from the group consisting of the homopolymers of propylene, represented by isotactic polypropylene, syndiotactic and partially iso- or syndio-tactic polypropylene, isotactic or partially isotactic polybutene-1 and poly-4-methylpentene-1, atactic polypropylene, propylene polymers known as polypropylene with a high degree of molecular branching, random copolymers of propylene and α -olefins having a number of carbon atoms ≥ 4 , such as the propylene-butene-1 ones.
7. Compositions according to claim 4, wherein the polyolefin-type thermoplastic polymer is selected from the group consisting of the amorphous or semicrystalline copolymers of ethylene with propylene having different ethylene-to-propylene ratio and random or block distribution of both comonomers, blends of the ethylene polymers listed in claim 5, the polymeric alloys among the ethylene and/or propylene polymers listed in claims 4 and 6 and/or the ethylene-propylene copolymers said above in this claim 7, and/or ethylene-propylene-diene terpolymers (EPDM rubbers).
8. Compositions according to claim 4, wherein the polyolefin-type thermoplastic polymer is selected from the group consisting of the linear homo-, co- and ter-polyolefins having a controlled molecular weight distribution, attainable by using metallocene catalysts.
9. Compositions according to claim 8, wherein the co- and ter-polyolefins having a controlled molecular weight distribution are selected from the group consisting of the copolymers and terpolymers of ethylene with one or respectively two linear α -olefins having a number of carbon atoms in the range of from 4 to 18.
10. Compositions according to claim 4, wherein the polyolefin-type thermoplastic polymer is selected from the group consisting of the copolymers and terpolymers of α -olefins with unsaturated comonomers containing more than one unsaturation of olefinic type, or one unsaturation of olefinic type and one or more functional groups, as well as the polymeric products deriving from homo-, co- or ter-polymers of α -olefins by grafting onto them comonomers containing both one unsaturation of olefinic type and one or more functional groups.
11. Compositions according to claim 4, wherein the polyolefin-type thermoplastic polymer is selected from the group consisting of polyethylene (particularly LDPE and

HDPE) and ethylene-propylene copolymers grafted with vinyltrialkoxysilanes, such as vinyltrimethoxysilane, as well as the copolymers deriving from direct copolymerization of ethylene with a vinyltrialkoxysilane, such as vinyltrimethoxysilane, post-crosslinkable in the solid state by hot water or steam treatments in the presence of known catalysts, pre-admixed in the molten material.

12. Compositions according to claim 10, wherein the polyolefin-type thermoplastic polymer is selected from the group consisting of the products attainable by grafting vinyl-type compounds containing epoxy groups, such as glycidylacrylate and glycidylmethacrylate, onto homo-, co- and ter-polymers of α -olefins such as ethylene and propylene, crosslinkable by catalysts and/or crosslinking agents known in epoxy resins chemistry.

13. Compositions according to claim 10, wherein the polyolefin-type thermoplastic polymer is selected from the group consisting of the copolymers of ethylene with non-conjugated linear dienes, such as 1,7-octadiene, 1,9-decadiene and 1,13-tetradecadiene, or copolymers of propylene with branched non-conjugated dienes, such as 6-methyl-1,6-octadiene or 7-methyl-1,6-octadiene, copolymers containing free olefinic unsaturations and post-crosslinkable through the introduction of free-radical initiators and optionally with the aid of bi- or tri-vinyl-functional monomers, such as 1,4-butanediol or 1,6-hexanediol diacrylates or dimethacrylates, neopentylglycol diacrylate or dimethacrylate, trimethylolpropane triacrylate or trimethacrylate, triallyl-cyanurate or -isocyanurate, triallyl-1,3,5-benzenecarboxylate.

14. Compositions according to claim 10, wherein the polyolefin-type thermoplastic polymer is selected from the group consisting of the thermoplastic copolymers and terpolymers among one or respectively two α -olefins and carboxylic acids containing one unsaturation of olefinic type, such as ethylene-acrylic acid and ethylene-methacrylic acid copolymers, containing an overall amount of said acid comonomers not exceeding 2.5% by weight.

15. Compositions according to claim 10, wherein the polyolefin-type thermoplastic polymer is selected from the group consisting of the homo-, co- and ter-polymers of α -olefins grafted by monocarboxylic acids containing one unsaturation of olefinic type, such as acrylic acid, methacrylic acid, monoalkylmaleates or monoalkylitaconates, or anhydrides of unsaturated bicarboxylic acids such as maleic anhydride or itaconic anhydride, and containing an overall amount of such grafting agents of acid type not

exceeding 1.5% by weight.

16. Compositions according to claim 1 or 2, wherein the thermoplastic polyolefin material, or component "A", consists of a physical mixture of two or more different polyolefin-type thermoplastic polymers selected from the group disclosed in claims
5 from 4 to 15.

17. Compositions according to claim 1 or 2, wherein the thermoplastic polyolefin material, or component "A", consists of a polyolefin-type thermoplastic polymer as disclosed in claim 3, or a mixture of two or more different polyolefin-type thermoplastic polymers as disclosed in claim 16, containing chemical agents selected from the group
10 consisting of free-radical initiators, catalysts, chemical co-reactants and/or mixtures thereof, suited to promote or cause the partial or total crosslinking of the same polyolefin material.

18. Compositions according to any of the preceding claims, wherein the component "B" consists of a metal powder or a mixture of different metal powders, consisting of metal
15 particles of small size and having a lamellar, acicular, fibrillar, dendritic, spherical, spheroidal, clavicular shape, or having an irregular shape with smooth or crater-rich surfaces, or having an irregular and complex shape such as small cavernous bodies or containing a plurality of micro-cavities, or consisting of hollow spherical or spheroidal particles, or a mixture thereof.

19. Compositions according to claim 18, wherein the component "B" comprises metal
20 powders characterized by particles having lamellar, acicular, fibrillar, dendritic shape, by particles being small cavernous bodies or containing micro-cavities, or mixtures among such powders and powders having particles of spheroidal and/or clavicular shape.

20. Compositions according to any of the preceding claims, wherein the metal powders
25 of component "B" consist of a single metal or an alloy of different metals, a metal or a metal alloy, the particles of which are coated by a thin layer of a different metal or metal alloy, or also a non-metallic mineral powder the particles of which are coated by a thin layer of a metal or metal alloy.

21. Compositions according to any of the preceding claims, wherein the metal powders
30 of component "B" are selected from the group consisting of aluminum, copper, iron, nickel or silver powders, as well as from the group consisting of brasses, bronzes and aluminum alloys.

22. Compositions according to claim 21, wherein the metal powders of component "B" are selected from the group consisting of aluminum powders, optionally in admixture with brass or bronze powders.
23. Compositions according to any of the preceding claims, wherein the metal powders
5 of component "B" are selected from the group consisting of silvered aluminum, copper or nickel powders, aluminum-coated milled glass fibers, glass micro-beads or hollow micro-spheres, silvered milled glass fibers, micro-beads, hollow micro-spheres, micro-flakes or ground glass powders, silvered mica powders, nickel-plated iron micro-grains.
24. Compositions according to any of the preceding claims, wherein the particles of the
10 metal powders of component "B" have sizes comprised in the range of from 0.1 to 200 μm .
25. Compositions according to claim 24, wherein the particles of the metal powders of component "B" have average size comprised in the range of from 1 to 100 μm , and preferentially of from 5 to 80 μm .
- 15 26. Compositions according to any of the preceding claims, wherein component "C" is a tertiary phosphine or amine, or a mixture of two or more different tertiary phosphines and/or amines, solid or liquid at room temperature.
27. Compositions according to any of the preceding claims, wherein component "C" consists of a tertiary phosphine or amine, or a mixture of two or more different tertiary
20 phosphines and/or amines, solid at room temperature and having a melting or complete liquefaction point not exceeding 250°C.
28. Compositions according to claim 27, wherein component "C" consists of a tertiary phosphine or amine, or a mixture of two or more different tertiary phosphines and/or amines, solid at a temperature of up to 50°C and having a melting or complete
25 liquefaction point not exceeding 180°C.
29. Compositions according to any of the preceding claims, wherein component "C" consists of a tertiary phosphine of general formula $\text{PY}_1\text{Y}_2\text{Y}_3$, wherein Y_1 , Y_2 and Y_3 have the meanings outlined in claim 1.
- 30 30. Compositions according to claim 29, wherein component "C" consists of a tertiary phosphine selected from the group consisting of triphenylphosphine, tri-*ortho*-tolylphosphine, tri-*meta*-tolylphosphine, tri-*para*-tolylphosphine, tri(4-ethylphenyl)phosphine, (*para*-tolyl)-diphenylphosphine, α -naphthyl-diphenylphosphine, β -naphthyl-diphenylphosphine, α -naphthyl-di(*para*-tolyl)phosphine, (*para*-

phenoxyphenyl)-diphenylphosphine, tri(4-ethylphenyl)phosphine, 4-ethylphenyl-diphenylphosphine, tri(3-methoxyphenyl)-phosphine, 3-methoxyphenyl-diphenylphosphine, di(4-methoxyphenyl)-phenylphosphine, 3-ethoxyphenyl-diphenylphosphine, 4-ethoxyphenyl-diphenylphosphine, benzyldiphenylphosphine, α -naphthylmethyl-diphenylphosphine, β -naphthylmethyl-diphenylphosphine, 4-methylbenzyl-diphenylphosphine, benzidryl-diphenylphosphine, α -naphthyl-dibenzylphosphine, di(α -naphthylmethyl)-phenylphosphine, di(β -naphthylmethyl)-phenylphosphine, and mixtures thereof.

31. Compositions according to any of the preceding claims, wherein component "C" consists of a tertiary amine of general formula $NY_1Y_2Y_3$, wherein Y_1 , Y_2 and Y_3 have the meanings outlined in claim 1.

32. Compositions according to claim 31, wherein component "C" consists of a tertiary amine selected from the group consisting of tribenzylamine, tri(4-methylbenzyl)amine, tri(3,4-dimethylbenzyl)amine, α -naphthylmethyl-dibenzylamine, β -naphthylmethyl-dibenzylamine, N-phenyl-dibenzylamine, N-(*para*-tolyl)-dibenzylamine, N-phenyl-di(4-methylbenzyl)amine, N-(4-ethylphenyl)-dibenzylamine, N-(4-butylphenyl)-dibenzylamine, triphenylamine, tri-*para*-tolylamine, tri-*para*-biphenylamine, N,N-dibenzyl-*meta*-anisidine, N,N-dibenzyl-*para*-anisidine, N-(3,5-dimethylphenyl)-dibenzylamine, N-phenyl-N-(α -naphthylmethyl)-benzylamine, and mixtures thereof.

33. Compositions according to any of the preceding claims, wherein component "D" consists of a mono-, di- or polybasic organic or inorganic protic acid having an acid equivalent weight comprised in the range of from 25 to 8000, and preferentially in the range of from 25 to 3000, or of a mixture of two or more different mono-, di- or polybasic organic or inorganic protic acids the average acid equivalent weight of which is in the range of from 25 to 8000, and preferentially in the range of from 25 to 3000.

34. Compositions according to claim 33, wherein the protic acid of component "D" consists of an organic protic acid selected from the group consisting of mono-, di- or polycarboxylic acids, alkane-, arene- and alkylarenesulfonic acids, and monoarene- and diarenephosphonic acids.

35. Compositions according to claim 34, wherein the protic acid of component "D" consists of a monocarboxylic acid which is a saturated fatty acid having a number of carbon atoms higher than or equal to 6, preferentially in the range of from 12 to 24, and preferentially selected from the group consisting of lauric, myristic, palmitic, stearic,

arachidic, behenic, lignoceric acids, or a mixture thereof, or consists of a mono- or polyunsaturated, monocarboxylic acid having a number of carbon atoms higher than or equal to 18, and preferentially selected from the group consisting of oleic, elaidic, erucic, linoleic, linolenic acids, or a mixture thereof, or still consists of a mixture of the latter acids and saturated fatty acids among those mentioned above.

36. Compositions according to claim 34, wherein the protic acid of component "D" consists of a bi- or polycarboxylic acid selected from the group consisting of succinic, maleic, fumaric, itaconic, glutaric and adipic acids, orthophthalic and isophthalic acids, trimellitic acid, pyromellitic acid and alkenylsuccinic acids, such as octenylsuccinic, decenylsuccinic and dodecenylsuccinic acids, the isomers and the isomeric mixtures of 2-octen-1-ylsuccinic acid and 2-dodecen-1-ylsuccinic acid.

37. Compositions according to claim 34, wherein the protic acid of component "D" is selected from the group consisting of alkanesulfonic, arenesulfonic and alkylarenesulfonic acids having a number of carbon atoms higher than or equal to 6, and preferentially in the range of from 12 to 34, such as dodecanesulfonic, hexadecanesulfonic, octadecanesulfonic, benzenesulfonic, *para*-toluenesulfonic acids, as well as the isomers of dodecylbenzenesulfonic and benzenedisulfonic acids.

38. Compositions according to claim 33, wherein the protic acid of component "D" is selected from the group consisting of polycarboxylic acids having a polymeric nature and an average acid equivalent weight lower than the above mentioned limit of 8000, and preferentially lower than 3000.

39. Compositions according to claim 38, wherein the protic acid of component "D" is selected from the group consisting of the following ones: copolymers and terpolymers of α -olefins with unsaturated carboxylic acids, such as the ethylene-acrylic acid and ethylene-methacrylic acid copolymers containing a weight portion of acrylic or methacrylic acid higher than or equal to 5%, and preferentially in the range of from 5 to 25%; oxidized polyethylene having an average acid equivalent weight lower than 1800; terpolymers of ethylene with one polar vinyl comonomer and acrylic or methacrylic acid, such as ethylene-methylacrylate-acrylic acid and ethylene-vinylacetate-methacrylic acid terpolymers.

40. Compositions according to claim 33, wherein the protic acid of component "D" consists of an inorganic protic acid selected from the group consisting of orthophosphoric acid, pyrophosphoric acid, polyphosphoric acids and orthophosphorous

acid.

41. Compositions according to any of the preceding claims, wherein the concentration of component "A" ranges from 57 to 99% of the total weight; the concentration of component "B" ranges from 0.9 to 25% of the total weight; the concentration of component "C" ranges from 0.1 to 8% of the total weight, while component "D" is introduced into the compositions in a weight percentage of the overall composition such that the relevant number of acid equivalents ranges from 0 to 200% of the total number of tertiary phosphine or amine equivalents, or of the sum of tertiary phosphine and amine equivalents, contained in the weight portion of component "C".

42. Process for forming and subsequent post-processing of the thermoplastic polymeric compositions disclosed in any of the preceding claims, which comprises:

- i) mixing components "B", "C" and "D" with component "A" in the molten state;
- ii) forming the composition into a semifinished object in the molten or plastic state, followed by solidification by natural or artificial cooling;
- iii) placing the solid semifinished object in, or passing it through, a microwave heating device working with a radiation frequency in the range of from 0.3 to 30 GHz, or a simultaneous microwave and infrared radiation heating device, with simultaneous or immediately subsequent post-processing consisting in the action of mechanical stresses which hot deform or form the object, or a part thereof, in a desired way;
- iv) extracting or driving off the object processed and still hot from the device, and natural or artificially accelerated cooling thereof.

43. Process according to claim 42, wherein the mixing step (i) is carried out by continuous mixing machines for polymeric materials in the molten state, machines selected from the group consisting of twin-screw extruders with co-rotating and intermeshing screws, counter-rotating and intermeshing screws, counter-rotating and non-intermeshing screws, twin-screw extruders with counter-rotating and non-intermeshing screws bearing mixing rotors of Banbury type, single-screw extruders.

44. Process according to claim 42 or 43, wherein the step (ii) for the semifinished article forming is carried out by injection molding, co-injection molding of different materials, conventional or dynamic extrusion, conventional or dynamic co-extrusion of different materials, optionally followed by hot processing operations selected from the group consisting of calendering, embossing, transit between rolls bearing grooves, teeth, figures in relief or intaglio figures, punches, dinking dies, or by cold processing

operations selected from the group consisting of drilling, milling, turning.

45. Process according to any of the claims from 42 to 44, wherein the microwave irradiation step (iii) is carried out by devices selected from the group consisting of multimode or single-mode resonant cavity devices, travelling or resonant waveguide
5 devices, direct irradiation devices, or combinations thereof.

46. Process according to any of the claims from 42 to 45, wherein the microwave irradiation step (iii) is carried in combination with a subsidiary heating or thermostating source working by blowing in, or by forced circulation of, air, other gases or vapors.

47. Process according to any of the claims from 42 to 46, wherein the microwave
10 irradiation step (iii) is carried out in combination with a simultaneous infrared irradiation:

- a) in the post-processing operations of the (iii) step being performed in microwave irradiation devices in ambient air with no aid by hot air, gases and/or vapors as a supplementary source for heating the surfaces of the articles being treated;
- 15 b) in the post-processing operations under microwave irradiation concerning semifinished articles characterized by high surface-to-volume ratios.

48. Process according to any of the claims from 42 to 47, wherein the infrared irradiation devices are selected from the group consisting of armored electric resistors, metal or silicon carbide electric resistors protected by metal grids, and static bodies made of inert
20 materials per se microwave-heatable and heated by the same electromagnetic microwave field devoted to heat the semifinished article.

49. Process according to any of the claims from 42 to 48, wherein the infrared irradiation devices are maintained at temperatures in the range of from 100 to 250°C.

50. Process according to any of the claims from 42 to 49, wherein the post-processing
25 operations of step (iii) are carried out by pneumatic or mechanical clamps, grips and forceps, friction rolls, pistons, punches, plane plates, molds and counter-molds, conical or cylindroconical drawing dies, pressure rolls having smooth or grooved surface, or also bearing figures in relief or intaglio figures.

51. Use of the thermoplastic polymeric compositions disclosed in any of the preceding
30 claims from 1 to 41, for the manufacture of nets, grids, geo-nets, geo-grids, and other bi- or tri-dimensional network structures by uni- or bi-axial stretching of sheets, slabs or preforms having a planar or tri-dimensional conformation, deriving by conventional or dynamic extrusion or co-extrusion, and endowed with predetermined spatial

distributions of holes, cavities, depressions, localized reliefs and/or protrusions.

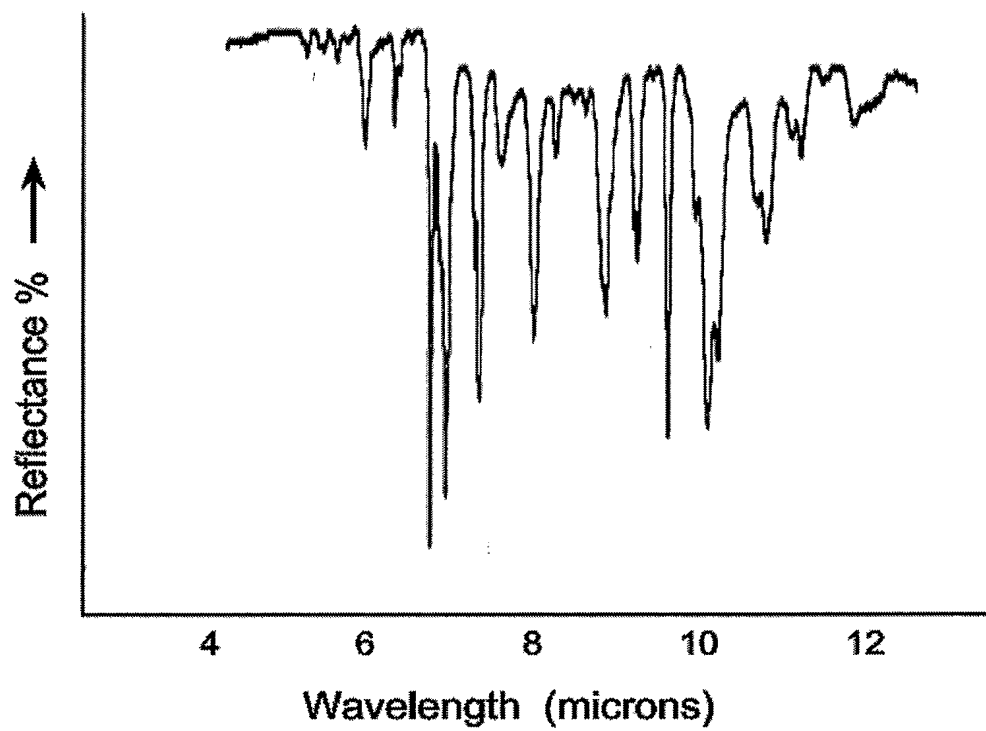
52. Use of the thermoplastic polymeric compositions disclosed in any of the preceding claims from 1 to 41 as welding materials rapidly meltable under microwave irradiation, for the super-fast joining of objects, parts or components made of different conventional polyolefin materials.

53. Use of the thermoplastic polymeric compositions disclosed in any of the preceding claims from 1 to 41, for the manufacture of semifinished articles having a composite polymeric structure, comprising parts or components made of a rapidly microwave-heatable polyolefin material and parts or components made of one or more conventional polyolefin materials which are non-microwave heatable, parts or components with a different composition being in contact, welded or variously interpenetrated with each other.

54. Thermoplastic polymeric compositions as herein disclosed and claimed.

55. Process for forming and subsequent post-processing of thermoplastic polymeric compositions as herein disclosed and claimed.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/IT 03/00746

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L23/00 B29C35/02 H05B6/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L B29C C08K H05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 329 475 A (SANYO CHEMICAL IND LTD) 23 August 1989 (1989-08-23) the whole document	1-41, 50-55
X	US 5 432 224 A (RYUHG OH JIROH ET AL) 11 July 1995 (1995-07-11) the whole document	1-41, 50-55
X	WO 98/14314 A (KENIG SHMUEL ; DODIUK KENIG HANNA (IL); MAROOFIAN IRA (US); HPM STADCO) 9 April 1998 (1998-04-09) the whole document	1-46, 50-55



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

20 April 2004

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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